Supporting Information

Iridium-Catalyzed Direct C–H Amidation of Anilines with Sulfonyl Azides: Easy Access to 1,2-Diaminobenzenes

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1. General information

Unless otherwise stated, all commercial materials and solvents were used directly without further purification. Melting points were determined in open glass capillaries and were uncorrected. $^1$H NMR spectra were recorded on 400 MHz spectrometers, and $^{13}$C NMR spectra were recorded on a 100 MHz spectrometer. Chemical shifts ($\delta$ in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl$_3$ or [d]$_6$-DMSO as an internal standard at room temperature. $^{13}$C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$ or [d]$_6$-DMSO. High-resolution mass spectra (HRMS) were equipped with an ESI source and a TOF detector. Column chromatography was performed on silica gel (70–230 mesh ASTM) using the reported eluents. Thin-layer chromatography (TLC) was carried out on 4×15 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254).

Aniline compounds 1a-j$^1$, 1a$^2$ and 1k$^3$, and sulfonyl azides 2b-m$^4$ were prepared according to the known procedures.

2. The Representative procedure for the synthesis of compounds 3

A flame-dried sealed tube was cooled to ambient temperature and filled with N$_2$. To this flask were added N-(o-tolyl)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol), para-toluenesulfonyl azide (2a) (118.2 mg, 0.6 mmol), [IrCl$_2$Cp$^*$]$_2$ (2.0 mg, 0.0025 mmol), AgSbF$_6$ (3.5 mg, 0.01 mmol) and 1,2-DCE (2.0 mL). Then the sealed tube was heated at 80 °C. After 12 h, the reaction mixture was cooled to ambient temperature, filtered through a pad of celite and silica gel, and washed with EtOAc (3 x 10 mL). The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired
product 3aa (175 mg, 99%) as a white solid.

3. Preparation and characterization of compounds 3

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\text{Synthesis of } 4\text{-methyl-}N\{3\text{-methyl-2-(pyrimidin-2-ylamino)phenyl}\text{benzenesulfonamide (3aa):}\n\]

The representative procedure was followed using \(N\)-(o-tolyl)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol) and para-toluenesulfonyl azide (2a) (118 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3aa (175 mg, 99%) as a white solid.

M. p. = 181–182 °C.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.29 \ (d, J = 4.8 \ \text{Hz}, 2\ H), 7.94 \ (\text{br s, } 1H), 7.57 \ (d, J = 8.1 \ \text{Hz}, 2H), 7.44 \ (d, J = 8.1 \ \text{Hz}, 1H), 7.21–7.15 \ (m, 3H), 7.07 \ (d, J = 7.5 \ \text{Hz}, 1H), 6.71 \ (t, J = 4.8 \ \text{Hz}, 1H), 6.70 \ (\text{br s, } 1H), 2.38 \ (\text{s, } 3H), 2.18 \ (\text{s, } 3H)\).

\(^1\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 160.9 \ (C_q), 158.6 \ (CH), 143.5 \ (C_q), 137.0 \ (C_q), 135.3 \ (C_q), 133.5 \ (C_q), 130.1 \ (C_q), 129.4 \ (CH), 127.9 \ (CH), 127.3 \ (CH), 127.1 \ (CH), 122.3 \ (CH), 112.6 \ (CH), 21.5 \ (CH_3), 18.5 \ (CH_3)\).

HRMS (ESI) m/z calcd for C\(_{18}\)H\(_{18}\)N\(_4\)O\(_2\)S [M + H]\(^+\): 355.1229, Found 355.1228.

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\text{Synthesis of } N\{3\text{-methoxy-2-(pyrimidin-2-ylamino)phenyl}\text{-4-methylbenzenesulfonamide (3ba):}\n\]
The representative procedure was followed using N-(2-methoxyphenyl)pyrimidin-2-amine (1b) (100.5 mg, 0.5 mmol) and para-toluenesulfonyl azide (2a) (118.2 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ba (180 mg, 97%) as a white solid.

M. p. = 188–189 °C.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 9.33 (br s, 1H), 8.39 (d, $J = 4.8$ Hz, 2H), 7.48 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 1H), 7.18–7.11 (m, 3H), 6.82 (br s, 1H), 6.79–6.73 (m, 2H), 3.80 (s, 3H), 2.37 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 160.7 (C$_q$), 158.4 (CH), 152.3 (C$_q$), 143.2 (C$_q$), 137.4 (C$_q$), 131.6 (C$_q$), 129.3 (CH), 126.9 (CH), 125.8 (CH), 122.5 (C$_q$), 118.8 (CH), 112.7 (CH), 108.1 (CH), 55.9 (CH$_3$), 21.5 (CH$_3$).

HRMS (ESI) m/z calcd for C$_{18}$H$_{19}$N$_4$O$_3$S [M + H]$^+$: 371.1178, Found 371.1178.

Synthesis of 4-methyl-N-{2-(pyrimidin-2-ylamino)-3-(trifluoromethyl)phenyl}benzenesulfonamide (3ca):

The representative procedure was followed using N-{2-(trifluoromethyl)phenyl}pyrimidin-2-amine (1c) (119.5 mg, 0.5 mmol) and para-toluenesulfonyl azide (2a) (118.2 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ca (192 mg, 94%) as a white solid.

M. p. = 197–198 °C.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 8.35 (d, $J = 4.8$ Hz, 2H), 7.97 (br s, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.51 (d, $J = 8.0$ Hz, 1H), 7.40 (dd, $J = 8.0, 8.0$ Hz, 1H), 7.20 (d, $J = 8.0$ Hz, 2H), 6.81 (t, $J = 4.8$ Hz, 1H), 6.58 (br s, 1H), 2.40 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 160.4 (C$_q$), 158.7 (CH), 143.9 (C$_q$), 136.6 (C$_q$), 135.3 (C$_q$), 129.5 (CH), 129.1 (CH), 127.2 (CH), 127.0 (CH), 126.7 (q, $^3$J$_{C-F} = 29$ Hz, C$_q$), 123.6 (q, $^3$J$_{C-F} = 276$ Hz, C$_q$), 123.6 (q, $^3$J$_{C-F} = 5$ Hz, CH), 113.6 (CH), 21.5 (CH$_3$) (One C$_q$ is invisible).
**Synthesis of N-[3-chloro-2-(pyrimidin-2-ylamino)phenyl]-4-methylbenzenesulfonamide (3da):**

The representative procedure was followed using N-(2-chlorophenyl)pyrimidin-2-amine (1d) (102.5 mg, 0.5 mmol), *para*-toluenesulfonyl azide (2a) (118.2 mg, 0.6 mmol), [IrCl₂Cp*]₂ (4.0 mg, 0.005 mmol) and AgSbF₆ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3da (184 mg, 98%) as a white solid.

M. p. = 203–204 °C.

**1H-NMR (400 MHz, CDCl₃):** δ = 8.57 (br s, 1H), 8.39 (d, *J* = 8.39 (d, *J* = 4.8 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.20 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.85 (br s, 1H), 6.83 (t, *J* = 4.9 Hz, 1H), 2.38 (s, 3H).

**13C-NMR (100 MHz, CDCl₃):** δ = 160.4 (Cₖ), 158.6 (CH), 143.6 (Cₗ), 136.9 (Cₖ), 133.8 (Cₗ), 130.0 (Cₖ), 129.7 (Cₗ), 129.4 (CH), 127.0 (CH), 126.9 (CH), 126.9 (CH), 124.6 (CH), 113.4 (CH), 21.5 (CH₃).


**Synthesis of 4-methyl-N-[2-(pyrimidin-2-ylamino)phenyl]benzenesulfonamide (3ea):**

The representative procedure was followed using N-phenylpyrimidin-2-amine (1e) (128.2 mg, 0.75 mmol), *para*-toluenesulfonyl azide (2a) (98.5 mg, 0.5 mmol), [IrCl₂Cp*]₂ (4.0 mg, 0.005 mmol) and AgSbF₆ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on
silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ea (115 mg, 68%) as a white solid.

M. p. = 209–210 °C.

1H-NMR (400 MHz, CDCl₃): δ = 8.37 (d, J = 4.8 Hz, 2H), 8.03 (br s, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 7.8 Hz, 1H), 7.44 (br s, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.23 (dd, J = 7.8, 7.5 Hz, 1H), 7.18-7.11 (m, 3H), 6.76 (t, J = 4.8 Hz, 1H), 2.33 (s, 3H).

13C-NMR (100 MHz, CDCl₃): δ = 160.2 (Cₗ), 158.3 (CH), 143.5 (Cₗ), 136.7 (Cₗ), 134.2 (Cₗ), 129.4 (CH), 129.3 (Cₗ), 127.8 (CH), 127.5 (CH), 127.1 (CH), 125.5 (CH), 123.8 (CH), 112.7 (CH), 21.5 (CH₃).


Synthesis of N-{5-chloro-2-(pyrimidin-2-ylamino)phenyl}-4-methylbenzenesulfonamide (3fa):
The representative procedure was followed using N-(4-chlorophenyl)pyrimidin-2-amine (1f) (153.8 mg, 0.75 mmol), para-toluenesulfonyl azide (2a) (98.5 mg, 0.5 mmol), [IrCl₂Cp*]₂ (4.0 mg, 0.005 mmol) and AgSbF₆ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3fa (130 mg, 69%) as a white solid.

M. p. = 223–224 °C.

1H-NMR (400 MHz, [d]₆-DMSO): δ = 9.80 (br s, 1H), 8.55 (br s, 1H), 8.37 (d, J = 4.8 Hz, 2H), 7.84 (d, J = 8.8 Hz, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.26 (dd, J = 8.8, 2.4 Hz, 1H), 7.13–7.07 (m, 3H), 6.85 (t, J = 4.8 Hz, 1H), 2.20 (s, 3H).

13C-NMR (100 MHz, [d]₆-DMSO): δ = 159.9 (Cₗ), 158.4 (CH), 143.7 (Cₗ), 136.5 (Cₗ), 134.1 (Cₗ), 129.9 (CH), 128.6 (Cₗ), 127.0 (CH), 127.0 (CH), 126.7 (Cₗ), 125.4 (CH), 113.6 (CH), 21.5 (CH₃)
(One CH is invisible).

Synthesis of $N$-{5-bromo-2-(pyrimidin-2-ylamino)phenyl}-4-methylbenzenesulfonamide (3ga):

The representative procedure was followed using $N$-(4-bromophenyl)pyrimidin-2-amine (1g) (187.5 mg, 0.75 mmol), para-toluenesulfonyl azide (2a) (98.5 mg, 0.5 mmol), [IrCl$_2$Cp*]$_2$ (4.0 mg, 0.005 mmol) and AgSbF$_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ga (180 mg, 86%) as a white solid.

M. p. = 220–221 °C.

$^1$H-NMR (400 MHz, [d]$_6$-DMSO): $\delta = 9.80$ (br s, 1H), 8.55 (br s, 1H), 8.37 (d, $J = 4.8$ Hz, 2H), 7.81 (d, $J = 8.8$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.37 (dd, $J = 8.8$, 2.2 Hz, 1H), 7.21 (d, $J = 2.2$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 2H), 6.84 (t, $J = 4.8$ Hz, 1H), 2.19 (s, 3H).

$^{13}$C-NMR (100 MHz, [d]$_6$-DMSO): $\delta = 159.8$ (C$_q$), 158.4 (CH), 143.7 (C$_q$), 136.5 (C$_q$), 134.6 (C$_q$), 130.0 (CH), 130.0 (CH), 129.8 (CH), 128.7 (C$_q$), 127.0 (CH), 125.5 (CH), 114.3 (C$_q$), 113.7 (CH), 21.5 (CH$_3$).

HRMS (ESI) m/z calcd for C$_{17}$H$_{16}$BrN$_4$O$_2$S [M + H]$^+$: 419.0177, Found 419.0173.

Synthesis of $N$-{5-iodo-2-(pyrimidin-2-ylamino)phenyl}-4-methylbenzenesulfonamide (3ha):

The representative procedure was followed using $N$-(4-iodophenyl)pyrimidin-2-amine (1h) (222.7 mg, 0.75 mmol), para-toluenesulfonyl azide (2a) (98.5 mg, 0.5 mmol), [IrCl$_2$Cp*]$_2$ (4.0 mg, 0.005 mmol) and AgSbF$_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ha (198 mg, 85%) as a
yellow solid.

M. p. = 205–206 °C.

\(^1\)H-NMR (400 MHz, [d]_6-DMSO): \(\delta = 9.73 \text{ (br s, 1H)}, 8.51 \text{ (br s, 1H)}, 8.38 \text{ (d, } J = 4.8 \text{ Hz, 2H}), 7.70 \text{ (d, } J = 8.7 \text{ Hz, 1H)}, 7.52 \text{ (dd, } J = 8.7, 1.7 \text{ Hz, 1H}), 7.44 \text{ (d, } J = 8.1 \text{ Hz, 2H}), 7.31 \text{ (s, 1H)}, 7.12 \text{ (d, } J = 8.1 \text{ Hz, 2H}), 6.85 \text{ (t, } J = 4.8 \text{ Hz, 1H}), 2.21 \text{ (s, 3H)}.

\(^1^3\)C-NMR (100 MHz, [d]_6-DMSO): \(\delta = 159.7 \text{ (C}_q\text{)}, 158.4 \text{ (CH)}, 143.7 \text{ (C}_q\text{)}, 136.5 \text{ (C}_q\text{)}, 136.1 \text{ (CH)}, 135.9 \text{ (CH)}, 135.4 \text{ (C}_q\text{)}, 129.8 \text{ (CH)}, 128.5 \text{ (C}_q\text{)}, 127.1 \text{ (CH)}, 125.5 \text{ (CH)}, 113.7 \text{ (CH)}, 85.8 \text{ (C}_q\text{)}, 21.5 \text{ (CH}_3\text{)}.

HRMS (ESI) m/z calcd for C\(_{17}\)H\(_{16}\)N\(_4\)O\(_2\)S [M + H]\(^+\): 467.0039, Found 467.0037.

![Chemical Structure](image)

**Synthesis of 4-methyl-N-[2-(pyrimidin-2-ylamino)-5-(trifluoromethyl)phenyl]benzenesulfonamide (3ia):**

The representative procedure was followed using N-[4-(trifluoromethyl)phenyl]pyrimidin-2-amine (1i) (179.2 mg, 0.75 mmol), para-toluenesulfonyl azide (2a) (98.5 mg, 0.5 mmol), [IrCl\(_2\)Cp\(*\)]\(_2\) (4.0 mg, 0.005 mmol) and AgSbF\(_6\) (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ia (149 mg, 73%) as a yellow solid.

M. p. = 199–200 °C.

\(^1\)H-NMR (400 MHz, [d]_6-DMSO): \(\delta = 9.90 \text{ (br s, 1H)}, 8.73 \text{ (br s, 1H)}, 8.46 \text{ (d, } J = 4.6 \text{ Hz, 2H}), 8.22 \text{ (d, } J = 8.0 \text{ Hz, 1H}), 7.57 \text{ (d, } J = 8.0 \text{ Hz, 1H}), 7.44 \text{ (d, } J = 8.0 \text{ Hz, 2H}), 7.22 \text{ (s, 1H)}, 7.14 \text{ (d, } J = 8.0 \text{ Hz, 2H}), 6.95 \text{ (t, } J = 4.6 \text{ Hz, 1H}), 2.20 \text{ (s, 3H)}.

\(^1^3\)C-NMR (100 MHz, [d]_6-DMSO): \(\delta = 159.4 \text{ (C}_q\text{)}, 158.6 \text{ (CH)}, 143.9 \text{ (C}_q\text{)}, 139.3 \text{ (C}_q\text{)}, 136.2 \text{ (C}_q\text{)}, 129.9 \text{ (CH)}, 127.1 \text{ (CH)}, 126.5 \text{ (C}_q\text{)}, 124.9 \text{ (q, } \frac{\beta}{\gamma}J_{C-F} = 4 \text{ Hz, CH}), 124.5 \text{ (q, } \frac{\beta}{\gamma}J_{C-F} = 4 \text{ Hz, CH}), 124.2 \text{ (q, } \frac{\beta}{\gamma}J_{C-F} = 259 \text{ Hz, C}_q\text{)}, 122.8 \text{ (CH)}, 122.7 \text{ (q, } \frac{\beta}{\gamma}J_{C-F} = 28 \text{ Hz, C}_q\text{)}, 114.4 \text{ (CH)}, 21.4 \text{ (CH}_3\text{)}.

\(^1^9\)F-NMR (376 MHz, [d]_6-DMSO): \(\delta = -60.6 \text{ (s)}\).
Synthesis of 4-methyl-N-{4-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ja):
The representative procedure was followed using N-(m-tolyl)pyrimidin-2-amine (1j) (92.5 mg, 0.5 mmol), para-toluenesulfonyl azide (2a) (118.2 mg, 0.6 mmol), [IrCl₂Cp*]₂ (4.0 mg, 0.005 mmol) and AgSbF₆ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ja (156 mg, 88%) as a white solid.
M. p. = 209–210 °C.

1H-NMR (400 MHz, CDCl₃): δ = 8.36 (d, J = 4.8 Hz, 2H), 7.90 (br s, 1H), 7.50 (d, J = 8.1 Hz, 2H), 7.35 (br s, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 7.8 Hz, 1H), 6.74 (t, J = 4.8 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H).

13C-NMR (100 MHz, CDCl₃): δ = 160.1 (Cₜₚ), 158.3 (CH), 143.4 (Cₚₜ), 137.8 (Cₚₚ), 136.7 (Cₚₚ), 134.2 (Cₚₚ), 129.4 (CH), 128.1 (CH), 127.2 (CH), 126.4 (Cₚₚ), 126.2 (CH), 124.1 (CH), 112.6 (CH), 21.5 (CH₃), 21.1 (CH₃).


Synthesis of N-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ab):
The representative procedure was followed using N-(o-tolyl)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol) and benzenesulfonyl azide (2b) (109.8 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ab
Synthesis of 4-methoxy-\(N\)-(3-methyl-2-(pyrimidin-2-ylamino)phenyl)benzenesulfonamide (3ac):
The representative procedure was followed using \(N\)-(o-tolyl)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol) and 4-methoxybenzenesulfonyl azide (2c) (127.8 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ac (183 mg, 99%) as a white solid.
M. p. = 194–195 °C.
\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.29 \text{ (d, } J = 4.8 \text{ Hz, 2H), 7.89 \text{ (br s, 1H), 7.61 \text{ (d, } J = 8.8 \text{ Hz, 2H), 7.44 \text{ (d, } J = 8.0 \text{ Hz, 1H), 7.17 \text{ (dd, } J = 8.0, 7.7 \text{ Hz, 1H), 7.07 \text{ (d, } J = 7.7 \text{ Hz, 1H), 6.85 \text{ (d, } J = 8.8 \text{ Hz, 2H), 6.74 \text{ (br s, 1H), 6.70 \text{ (t, } J = 4.8 \text{ Hz, 1H), 3.82 \text{ (s, 3H), 2.18 \text{ (s, 3H).}}}
\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 162.9 \text{ (C\(_q\)), 161.0 \text{ (C\(_q\)), 158.6 \text{ (CH), 135.3 \text{ (C\(_q\)), 133.6 \text{ (C\(_q\)), 131.5 \text{ (C\(_q\)), 130.1 \text{ (C\(_q\)), 129.2 \text{ (CH), 127.9 \text{ (CH), 127.3 \text{ (CH), 122.3 \text{ (CH), 114.0 \text{ (CH), 112.6 \text{ (CH), 55.5 \text{ (CH\(_3\))}, 18.6 \text{ (CH\(_3\))}}.}}
\text{HRMS (ESI) m/z calcd for C}_{18}\text{H}_{19}\text{N}_4\text{O}_{3}\text{S} [M + H]^+: 371.1178, Found 371.1177.}{
Synthesis of 4-fluoro-N-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ad):
The representative procedure was followed using N-(o-tolyl)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol) and 4-fluorobenzenesulfonyl azide (2d) (120.6 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ad (177 mg, 99%) as a white solid.
M. p. = 213–214 °C.

1H-NMR (400 MHz, [d]6-DMSO): \( \delta = 9.55 \) (br s, 1H), 8.34 (br s, 1H), 8.21 (d, \( J = 4.8 \) Hz, 2H), 7.63 (dd, \( J = 8.2, 7.4 \) Hz, 2H), 7.19 (dd, \( J = 7.8, 7.8 \) Hz, 1H), 7.15–7.01 (m, 4H), 6.68 (t, \( J = 4.8 \) Hz, 1H), 3.47 (s, 3H).

13C-NMR (100 MHz, [d]6-DMSO): \( \delta = 164.7 \) (d, \( 1J_{C-F} = 251 \) Hz, Cq), 161.1 (Cq), 158.3 (CH), 137.8 (Cq), 136.5 (d, \( 1J_{C-F} = 3 \) Hz, Cq), 132.9 (Cq), 131.9 (Cq), 129.9 (d, \( 3J_{C-F} = 10 \) Hz, CH), 128.3 (CH), 126.5 (CH), 122.7 (CH), 116.6 (d, \( 2J_{C-F} = 22 \) Hz, CH), 112.1 (CH), 19.0 (CH3).

19F-NMR (376 MHz, [d]6-DMSO): \( \delta = -106.3 \) (s).

Synthesis of 4-chloro-N-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ae):
The representative procedure was followed using N-(o-tolyl)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol) and 4-chlorobenzenesulfonyl azide (2e) (130.2 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ae (185 mg, 99%) as a white solid.
M. p. = 205–206 °C.
H-NMR (400 MHz, [d]$_6$-DMSO): $\delta = 9.60$ (br s, 1H), 8.31 (br s, 1H), 8.19 (d, $J = 4.8$ Hz, 2H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 7.8$ Hz, 1H), 7.11 (dd, $J = 7.8$, 7.6 Hz, 1H), 7.06 (d, $J = 7.6$ Hz, 1H), 6.69 (t, $J = 4.8$ Hz, 1H), 2.00 (s, 3H).

C-NMR (100 MHz, [d]$_6$-DMSO): $\delta = 161.0$ (C$_q$), 158.3 (CH), 138.9 (C$_q$), 137.9 (C$_q$), 137.8 (C$_q$), 132.7 (C$_q$), 132.0 (C$_q$), 129.5 (CH), 128.7 (CH), 128.4 (CH), 126.5 (CH), 122.9 (CH), 112.1 (CH), 19.0 (CH$_3$).

HRMS (ESI) m/z calcd for C$_{17}$H$_{16}$ClN$_5$O$_2$S [M + H]$^+$: 375.0682, Found 375.0683.

Synthesis of $N$-[3-methyl-2-(pyrimidin-2-ylamino)phenyl]-4-nitrobenzenesulfonamide (3af):

The representative procedure was followed using $N$-(o-tolyl)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol) and 4-nitrobenzenesulfonyl azide (2f) (136.8 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1$\rightarrow$5:1:1) to afford the desired product 3af (190 mg, 98%) as a pale yellow solid.

M. p. = 234–235 °C.

H-NMR (400 MHz, [d]$_6$-DMSO): $\delta = 9.82$ (br s, 1H), 8.26 (br s, 1H), 8.10 (d, $J = 4.8$ Hz, 2H), 8.06 (d, $J = 8.8$ Hz, 2H), 7.74 (d, $J = 8.8$ Hz, 2H), 7.24 (d, $J = 7.8$ Hz, 1H), 7.15 (dd, $J = 7.8$, 7.5 Hz, 1H), 7.10 (d, $J = 7.5$ Hz, 1H), 6.54 (t, $J = 4.8$ Hz, 1H), 1.96 (s, 3H).

C-NMR (100 MHz, [d]$_6$-DMSO): $\delta = 160.9$ (C$_q$), 158.2 (CH), 149.6 (C$_q$), 145.6 (C$_q$), 137.7 (C$_q$), 132.4 (C$_q$), 132.1 (C$_q$), 129.1 (CH), 128.3 (CH), 126.5 (CH), 124.8 (CH), 124.1 (CH), 112.0 (CH), 19.0 (CH$_3$).

HRMS (ESI) m/z calcd for C$_{17}$H$_{16}$N$_5$O$_2$S [M + H]$^+$: 386.0923, Found 386.0921.
Synthesis of 3-methyl-N-[3-methyl-2-(pyrimidin-2-ylamino)phenyl]benzenesulfonamide (3ag):
The representative procedure was followed using N-(o-tolyl)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol) and 3-methylbenzenesulfonyl azide (2g) (118.2 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ag (170 mg, 96%) as a white solid.
M. p. = 176−177 °C.

$^1$H-NMR (400 MHz, CDCl$_3$): δ = 8.33 (d, $J$ = 4.8 Hz, 2H), 7.98 (br s, 1H), 7.49−7.41 (m, 3H), 7.34 (d, $J$ = 7.2 Hz, 1H), 7.28 (d, $J$ = 7.2 Hz, 1H), 7.19 (dd, $J$ = 7.6, 7.6 Hz, 1H), 7.09 (d, $J$ = 7.6 Hz, 1H), 6.72 (t, $J$ = 4.8 Hz, 1H), 6.41 (br s, 1H), 2.33 (s, 3H), 2.18 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): δ = 160.8 (C$_q$), 158.6 (CH), 139.8 (C$_q$), 139.0 (C$_q$), 134.9 (C$_q$), 133.5 (CH), 133.2 (C$_q$), 130.5 (C$_q$), 128.6 (CH), 128.2 (CH), 127.4 (CH), 127.2 (CH), 124.2 (CH), 123.2 (CH), 112.6 (CH), 21.3 (CH$_3$), 18.5 (CH$_3$).
HRMS (ESI) m/z calcd for C$_{18}$H$_{19}$N$_4$O$_2$S [M + H]$^+$: 355.1229, Found 355.1230.

Synthesis of 3-fluoro-N-[3-methyl-2-(pyrimidin-2-ylamino)phenyl]benzenesulfonamide (3ah):
The representative procedure was followed using N-(o-tolyl)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol) and 3-fluorobenzenesulfonyl azide (2h) (120.6 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ah (138 mg, 77%) as a white solid.
M. p. = 192−193 °C.

$^1$H-NMR (400 MHz, CDCl$_3$): δ = 8.33 (d, $J$ = 4.8 Hz, 2H), 8.23 (br s, 1H), 7.45 (d, $J$ = 7.2 Hz, 1H), 7.45 (d, $J$ = 7.2 Hz, 1H), 7.39 (dd, $J$ = 7.8, 7.8 Hz, 1H), 7.34 (d, $J$ = 6.8 Hz, 1H), 7.23 (dd, $J$ = 7.7, 7.5 Hz, 1H), 7.19 (d, $J$ = 7.8 Hz, 1H), 7.11 (d, $J$ = 7.5 Hz, 1H), 6.75 (t, $J$ = 4.8 Hz, 1H), 6.57 (br s, 1H), 2.20 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): δ = 162.1 (d, $^1$J$_{C-F}$ = 251 Hz, C$_q$), 160.7 (C$_q$), 158.6 (CH), 142.1 (d,
$^3J_{C-F} = 7$ Hz, $C_q$, 134.7 ($C_q$), 132.6 ($C_q$), 130.6 ($C_q$), 130.5 (d, $^3J_{C-F} = 7$ Hz, CH), 128.5 (CH), 127.2 (CH), 123.3 (CH), 122.8 (d, $^4J_{C-F} = 3$ Hz, CH), 119.9 (d, $^2J_{C-F} = 21$ Hz, CH), 114.4 (d, $^2J_{C-F} = 24$ H, CH), 112.8 (CH), 18.5 (CH$_3$).

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta = -(119.7–110.0)$ (m).

HRMS (ESI) m/z calcd for C$_{17}$H$_{16}$FN$_4$O$_2$S [M + H]$^+$: 359.0978, Found 359.0978.

Synthesis of 3-chloro-N-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ai):

The representative procedure was followed using N-(o-tolyl)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol) and 3-chlorobenzenesulfonyl azide (2i) (130.5 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ai (186 mg, 99%) as a white solid.

M. p. = 183–184 °C.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 8.34$ (d, $J = 4.8$ Hz, 2H), 8.27 (s, 1H), 7.60 (br s, 1H), 7.53 (d, $J = 7.8$ Hz, 1H), 7.49 (d, $J = 7.9$, 1H), 7.45 (d, $J = 7.9$, 1H), 7.33 (d, $J = 7.9$, 7.9 Hz, 1H), 7.21 (dd, $J = 7.8$, 7.8 Hz, 1H), 7.12 (d, $J = 7.8$ Hz, 1H), 6.76 (t, $J = 4.8$ Hz, 1H), 6.53 (br s, 1H), 2.21 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 160.6$ ($C_q$), 158.6 (CH), 141.8 ($C_q$), 135.0 ($C_q$), 134.6 ($C_q$), 132.8 (CH), 132.5 ($C_q$), 130.8 ($C_q$), 130.0 (CH), 128.6 (CH), 127.1 (CH), 127.0 (CH), 125.1 (CH), 123.6 (CH), 112.8 (CH), 18.5 (CH$_3$).

HRMS (ESI) m/z calcd for C$_{17}$H$_{16}$ClN$_4$O$_2$S [M + H]$^+$: 375.0682, Found 375.0681.

Synthesis of 2-methyl-N-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3aj):
The representative procedure was followed using N-(o-tolyl)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol) and 2-methylbenzenesulfonyl azide (2j) (118.2 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3aj (175 mg, 99%) as a white solid.

M. p. = 164–165 °C.

1H-NMR (400 MHz, CDCl₃): δ = 8.35 (d, J = 4.8 Hz, 2H), 8.03 (br s, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.42 (dd, J = 7.4, 7.4 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.23 (dd, J = 7.8, 7.8 Hz, 1H), 7.13 (dd, J = 7.8, 7.8 Hz, 1H), 7.05 (d, J = 7.4 Hz, 1H), 6.74 (t, J = 4.8 Hz, 1H), 6.68 (br s, 1H), 2.46 (s, 3H), 2.19 (s, 3H).

13C-NMR (100 MHz, CDCl₃): δ = 161.1 (Cₐ), 158.6 (CH), 138.2 (Cₐ), 137.3 (Cₐ), 135.1 (Cₐ), 133.5 (Cₐ), 132.8 (CH), 132.5 (CH), 129.8 (Cₐ), 129.5 (CH), 127.7 (CH), 127.2 (CH), 126.1 (CH), 121.8 (CH), 112.7 (CH), 20.2 (CH₃), 18.5 (CH₃).


Synthesis of 2-fluoro-N-[3-methyl-2-(pyrimidin-2-ylamino)phenyl]benzenesulfonamide (3ak):
The representative procedure was followed using N-(o-tolyl)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol) and 2-fluorobenzenesulfonyl azide (2k) (120.6 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3ak (171 mg, 95%) as a white solid.

M. p. = 161–162 °C.

1H-NMR (400 MHz, CDCl₃): δ = 8.50 (br s, 1H), 8.33 (d, J = 4.8 Hz, 2H), 7.78 (dd, J = 7.8, 7.8 Hz, 1H), 7.51 (dd, J = 8.0, 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.17 (ddd, J = 7.8, 7.8, 2.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.09 (dd, J = 7.8, 4.5 Hz, 2H), 6.92 (br s, 1H), 6.75 (t, J = 4.8 Hz, 1H), 2.20 (s, 3H).

13C-NMR (100 MHz, CDCl₃): δ = 160.9 (Cₐ), 159.2 (d, 1J_C-F = 255 Hz, Cₐ), 158.6 (CH), 135.0 (d, 3J_C-F = 8 Hz, CH), 134.8 (Cₐ), 132.7 (Cₐ), 130.5 (Cₐ), 130.4 (CH), 128.3 (CH), 128.3 (d, 3J_C-F =
Synthesis of \(N\)-\{3-methyl-2-(pyrimidin-2-ylamino)phenyl\}-1-phenylmethanesulfonamide (3al):

The representative procedure was followed using \(N\)-(o-toly)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol) and phenylmethanesulfonyl azide (2l) (118.2 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3al (100 mg, 57%) as a white solid.

M. p. = 174−175 °C.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.19 \) (br s, 1H), 8.16 (d, \(J = 4.8 \) Hz, 2H), 7.51 (d, \(J = 8.0 \) Hz, 1H), 7.32−7.28 (m, 5H), 7.25 (dd, \(J = 8.0, 7.8 \) Hz, 1H), 7.12 (d, \(J = 7.6 \) Hz, 1H), 6.58 (t, \(J = 4.8 \) Hz, 1H), 6.52 (br s, 1H), 4.38 (s, 2H), 2.24 (s, 3H).

\(^13\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 161.1 \) (C\(_q\)), 158.3 (CH), 136.3 (C\(_q\)), 134.7 (C\(_q\)), 130.8 (CH), 128.8 (C\(_q\)), 128.8 (CH), 128.7 (CH), 128.6 (C\(_q\)), 127.8 (CH), 127.0 (CH), 119.4 (CH), 112.6 (CH), 58.4 (CH\(_3\)), 18.6 (CH\(_3\)).


Synthesis of \(N\)-\{3-methyl-2-(pyrimidin-2-ylamino)phenyl\}methanesulfonamide (3am):

The representative procedure was followed using \(N\)-(o-toly)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol) and methanesulfonyl azide (2m) (72.6 mg, 0.6 mmol). After 12 h, purification by column
chromatography on silica gel (PE/EtOAc/DCM = 10:1:1→5:1:1) to afford the desired product 3am (88 mg, 63%) as a white solid.

M. p. = 169–171 °C.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.35\) (d, \(J = 4.8\) Hz, 2H), 7.79 (br s, 1H), 7.53 (d, \(J = 8.0\) Hz, 1H), 7.26 (dd, \(J = 8.0, 8.0\) Hz, 1H), 7.16 (br s, 1H), 7.15 (d, \(J = 8.0\) Hz, 1H), 6.74 (t, \(J = 4.8\) Hz, 1H), 2.97 (s, 3H), 2.29 (s, 3H).

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 161.3\) (C\(_q\)), 158.7 (CH), 135.9 (C\(_q\)), 134.1 (C\(_q\)), 129.9 (C\(_q\)), 127.9 (CH), 127.7 (CH), 121.3 (CH), 113.0 (CH), 39.8 (CH\(_3\)), 18.6 (CH\(_3\)).

HRMS (ESI) m/z calcd for C\(_{12}\)H\(_{15}\)N\(_4\)O\(_2\)S [M + H]\(^+\): 279.0916, Found 279.0912.

Intermolecular competition experiment with anilines 1a and 1c (Scheme 4)
The mixture of \(N\)-(o-tolyl)pyrimidin-2-amine (1a) (185.0 mg, 1.0 mmol), \(N\)-{2-(trifluoromethyl)phenyl}pyrimidin-2-amine (1c) (239 mg, 1.0 mmol), \(para\)-toluenesulfonyl azide (2a) (98.5 mg, 0.5 mmol), \([IrCl_2Cp^*]_2\) (4.0 mg, 0.005 mmol), \(AgSbF_6\) (6.9 mg, 0.02 mmol) and 1,2-DCE (2.0 mL) was stirred at 80 °C under \(N_2\) for 12 h. The reaction mixture was cooled to ambient temperature, filtered through a pad of celite and silica gel, and washed with EtOAc (3 x 10 mL). The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 10:1:1→5:1:1→3:1:1) to yield 3ca (17 mg, 10%) as a pale yellow solid and 3aa (175 mg, 85%) as a white solid.
Intemolecular competition experiment with sulfonyl azides 2a and 2f (Scheme 5)

![Scheme 5](image)

The mixture of N-(o-tolyl)pyrimidin-2-amine (1a) (92.5 mg, 0.5 mmol), para-toluenesulfonyl azide (2a) (197.0 mg, 1.0 mmol), 4-nitrobenzenesulfonyl azide (2f) (228.0 mg, 1.0 mmol), [IrCl₂Cp*]₂ (4.0 mg, 0.005 mmol), AgSbF₆ (6.9 mg, 0.02 mmol) and 1,2-DCE (2.0 mL) was stirred at 80 °C under N₂ for 12 h. The reaction mixture was cooled to ambient temperature, filtered through a pad of celite and silica gel, and washed with EtOAc (3 x 10 mL). The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 10:1:1→5:1:1→3:1:1) to yield 3af (101 mg, 52%) as a pale yellow solid and 3aa (62 mg, 35%) as a white solid.
Iridium-catalyzed direct ortho-C–H amidation of sulfonyl azide 2a with aniline 1e in 1,2-DCE and [D]₄-AcOH (Scheme 6)

A mixture of N-phenylpyrimidin-2-amine (1e) (342.0 mg, 2.0 mmol), para-toluenesulfonyl azide (2a) (197.0 mg, 1.0 mmol), [IrCl₂Cp*]₂ (8.0 mg, 0.01 mmol), AgSbF₆ (13.8 mg, 0.04 mmol), 1,2-DCE (2.0 mL) and [D]₄-AcOH (112 μL, 2.0 mmol) was stirred at 80 °C under N₂ for 12 h. The reaction mixture was cooled to ambient temperature, filtered through a pad of celite and silica gel, and washed with EtOAc (3 x 10 mL). The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 40:1:1→10:1:1→4:1:1) to give [D]ₙ-1e (88 mg, 26%) as a white solid and [D]ₙ-3ea (144 mg, 42%) as a white solid. The deuterium incorporation was estimated by ¹H-NMR spectroscopy.
Removal of the 2-pyridyl and sulfonyl moieties (Scheme 8)\(^5\)

Synthesis of 3-methylbenzene-1,2-diamine (4aa/4ad):

**Procedure 1:** 4-Methyl-N-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3aa, 0.2 mmol, 71mg) was dissolved in aqueous HCl (37%, 2.0 mL) in a microwave vial. The vial was heated up to 150 °C (40 W) for 3 h in the microwave oven. The reaction mixture was allowed to cool to ambient temperature and poured into EtOAc (50 mL), and then saturated aqueous NaHCO\(_3\) solution was added until the pH was adjusted to 7. The aqueous layer was extracted with EtOAc (3 × 50 mL), the combined organic layers were dried with Na\(_2\)SO\(_4\) and concentrated \textit{in vacuo}. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 20:1:1→10:1:1→5:1:1) to give 4aa (13mg, 53%) as a yellow solid.

**Procedure 2:** 4-Methyl-N-{3-methyl-2-(pyrimidin-2-ylamino)phenyl}benzenesulfonamide (3ad, 0.2 mmol, 71mg) was dissolved in aqueous HCl (37%, 2.0 mL) in a microwave vial. The vial was heated up to 150 °C (40 W) for 3 h in the microwave oven. The reaction mixture was allowed to cool to ambient temperature and poured into EtOAc (50 mL), and then saturated aqueous NaHCO\(_3\) solution was added until the pH was adjusted to 7. The aqueous layer was extracted with EtOAc (3 × 50 mL), the combined organic layers were dried with Na\(_2\)SO\(_4\) and concentrated \textit{in vacuo}. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 20:1:1→10:1:1→5:1:1) to give 4aa (12mg, 48%) as a yellow solid.

M. p. = 70–71 °C.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 6.72–6.61 (m, 3H), 3.28 (br s, 2H), 3.28 (br s, 2H), 2.23 (s, 3H)\).

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 133.9 (C_3), 133.5 (C_3), 123.4 (C_3), 122.1 (CH), 119.2 (CH), 115.1 (CH), 17.4 (CH\(_3\)).\)

HRMS (ESI) m/z calcd for C\(_{34}\)H\(_{25}\)O [M + H]: 123.0917, Found 123.0917.

Synthesis of benzene-1,2-diamine (4ea):
4-Methyl-N-[2-(pyrimidin-2-ylamino)phenyl]benzenesulfonamide (3ea, 0.2 mmol, 68mg) was dissolved in aqueous HCl (37%, 2.0 mL) in a microwave vial. The vial was heated up to 150 °C (40 W) for 3 h in the microwave oven. The reaction mixture was allowed to cool to ambient temperature and poured into EtOAc (50 mL), and then saturated aqueous NaHCO₃ solution was added until the pH was adjusted to 7. The aqueous layer was extracted with EtOAc (3 × 50 mL), the combined organic layers were dried with Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 30:1:1→10:1:1→6:1:1) to give 4ea (13mg, 58%) as a yellow solid. M. p. = 103–105 °C.

1H-NMR (400 MHz, CDCl₃): δ = 6.79–6.70 (m, 4H), 3.33 (br s, 4H).

13C-NMR (100 MHz, CDCl₃): δ = 134.8 (C₉), 120.3 (CH), 116.8 (CH).


Synthesis of 4-(trifluoromethyl)benzene-1,2-diamine (4ia):

4-Methyl-N-[2-(pyrimidin-2-ylamino)-5-(trifluoromethyl)phenyl]benzenesulfonamide (3ia, 0.2 mmol, 82mg) was dissolved in aqueous HCl (37%, 2.0 mL) in a microwave vial. The vial was heated up to 150 °C (40 W) for 3 h in the microwave oven. The reaction mixture was allowed to cool to ambient temperature and poured into EtOAc (50 mL), and then saturated aqueous NaHCO₃ solution was added until the pH was adjusted to 7. The aqueous layer was extracted with EtOAc (3 × 50 mL), the combined organic layers were dried with Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 20:1:1→10:1:1→5:1:1) to give 4ia (19mg, 54%) as a white solid. M. p. = 57–58 °C.

1H-NMR (400 MHz, CDCl₃): δ = 7.01 (d, J = 7.8 Hz, 1H), 6.95 (s, 1H), 6.73 (d, J = 7.8 Hz, 1H), 3.56 (br s, 2H), 3.56 (br s, 2H).

13C-NMR (100 MHz, CDCl₃): δ = 138.2 (C₉), 134.1 (C₉), 124.7 (q, ¹JC₁-F = 269 Hz, C₉), 121.8 (q, ²JC₁-F = 269 Hz, C₉), 124.7 (q, ³JC₁-F = 269 Hz, C₉), 117.7 (q, ⁴JC₁-F = 4 Hz, CH), 115.5 (CH), 113.5 (q, ⁵JC₁-F = 4 Hz, CH).
$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta = -61.3$ (s).

HRMS (ESI) m/z calcd for C$_{14}$H$_{25}$O [M + H]$^+$: 177.0634, Found 177.0634.
References


NMR spectra of compounds 3 and 4

3aa
(\textsuperscript{1}H NMR, CDCl\textsubscript{3})
$^{13}$C NMR, CDCl$_3$)

3aa

$^1$H NMR, CDCl$_3$)

3ba
3ba
($^{13}$C NMR, CDCl$_3$)

3ca
($^1$H NMR, CDCl$_3$)
\[ \text{3ca} \quad (^{13}\text{C NMR, CDCl}_3) \]

\[ \text{3da} \quad (^{1}\text{H NMR, CDCl}_3) \]
3da
($^{13}$C NMR, CDCl$_3$)

3ea
($^1$H NMR, CDCl$_3$)
3ea
($^{13}$C NMR, CDCl$_3$)

3fa
($^1$H NMR, CDCl$_3$)
3fa
($^{13}$C NMR, CDCl$_3$)

3ga
($^1$H NMR, [d]$_6$-DMSO)
3ga
$^{13}$C NMR, [d$_6$]-DMSO

3ha
$^1$H NMR, [d$_6$]-DMSO
3ha
\((^{13}\text{C NMR, [d]}_6\text{-DMSO})\)

3ia
\((^{1}\text{H NMR, [d]}_6\text{-DMSO})\)
3ia
($^{13}$C NMR, [d]$_6$-DMSO)

3ja
($^1$H NMR, CDCl$_3$)
3ac
($^{13}$C NMR, CDCl$_3$)

3ad
($^1$H NMR, [d]$_6$DMSO)
$\text{3ad}$

$(^{13}\text{C NMR, } [d]_{60}\text{-DMSO})$

$\text{3ae}$

$(^{1}\text{H NMR, } [d]_{60}\text{-DMSO})$
3af
($^{13}$C NMR, [d$_6$]-DMSO)

3ag
($^1$H NMR, CDCl$_3$)
3ah
\(^{13}\text{C NMR, CDCl}_3\)

3ai
\(^{1}\text{H NMR, CDCl}_3\)
3ai
($^{13}$C NMR, CDCl$_3$)

3aj
($^1$H NMR, CDCl$_3$)
3aj
($^{13}$C NMR, CDCl$_3$)

3ak
($^1$H NMR, CDCl$_3$)
$3ak$  
($^{13}$C NMR, CDCl$_3$)

$3al$  
($^1$H NMR, CDCl$_3$)
$f_1$ (ppm)

$0.5$  
$1.0$  
$1.5$  
$2.0$  
$2.5$  
$3.0$  
$3.5$  
$4.0$  
$4.5$  
$5.0$  
$5.5$  
$6.0$  
$6.5$  

$18.6$  
$39.8$  
$113.0$  
$121.3$  
$127.7$  
$127.9$  
$129.9$  
$134.1$  
$135.9$  
$158.7$  
$161.3$

$3am$  
($^{13}$C NMR, CDCl$_3$)

$4aa/4ad$  
($^1$H NMR, CDCl$_3$)
4aa/4ad
($^{13}$C NMR, CDCl$_3$)

4ea
($^1$H NMR, CDCl$_3$)
4ea
\((^{13}\text{C} \text{ NMR, CDCl}_3)\)

4ia
\((^{1}\text{H} \text{ NMR, CDCl}_3)\)
4ia
($^{13}$C NMR, CDCl$_3$)