Supporting Information for

Efficient 2-Sulfolmethyl Quinoline Formation from 2-Methylquinolines and Sodium Sulfinites under Transition-Metal Free Conditions

Fuhong Xiao,*a Shuqing Chen,a Ya Chen,a Huawen Huang*a and Guo-Jun Deng*a

a Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China; Fax: (+86)-731-58292251; e-mail: 494707822@163.com; gideng@xtu.edu.cn

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General information:

All experiments were carried out under an atmosphere of air. Flash column chromatography was performed over silica gel 48-75 μm. ¹H NMR and ¹³C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to SiMe₄ or chloroform signals. MS analyses were performed on an Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded at Institute of Chemistry, Chinese Academy of Sciences. The structures of known compounds were further corroborated by comparing their NMR data and MS data with those of literature. Reagents were used as received or prepared by our laboratory.

Optimization of reaction conditions

Table S1. Optimization of reaction conditions

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* Reaction conditions: 1a (0.5 mmol), 2a (1.25 mmol), catalyst (0.5 mmol, for I₂ 0.25 mmol), oxidant (0.5 mmol), solvent (1.6 mL), 80 °C, 16 h under air. ² GC yield based on 1a. ³ 40 °C. ⁴ KI (0.25 mmol). ⁵ 0.25 mmol TBHP.
Optimization of reaction conditions under oxygen atmosphere

Table S2. Optimization of reaction conditions under oxygen atmosphere \(^a\)

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\(^a\) Reaction conditions: 1a (0.5 mmol), 2a (1.25 mmol), catalyst (0.5 mmol, for I\(_2\) 0.25 mmol), solvent (1.6 mL), 80 °C, 16 h under O\(_2\). \(^b\) GC yield based on 1a. \(^c\) 100 °C. \(^d\) TBHP (0.25 mmol). \(^e\) 24 h.

General procedure for the control experiments:

A 10 mL oven-dried reaction vessel was charged with sodium benzenesulfinate (2a, 205 mg, 1.25 mmol), KI (83.3 mg, 0.5 mmol), 2, 2, 6, 6-tetramethyl-1-piperidinyloxy (78 mg, 0.5 mmol), 2-methylquinoline (1a, 67.5 μL, 0.5 mmol), acetic acid (0.8 mL) and DMSO (0.8 mL) under air. Finally TBHP (75 μL, 0.5 mmol) was slowly added to the reaction vessel by syringe. The resulting solution was stirred at 80 °C for 16 h, and no desired product 3a was observed.
A 10 mL oven-dried reaction vessel was charged with KI (83.3 mg, 0.5 mmol), 2-methylquinoline (1a, 67.5 μL, 0.5 mmol), acetic acid (0.8 mL) and DMSO (0.8 mL) under air. Finally TBHP (75 μL, 0.5 mmol) was slowly added to the reaction vessel by syringe. The resulting solution was stirred at 80 °C for 16 h, and no 2-(iodomethyl)quinoline was observed.

A 10 mL oven-dried reaction vessel was charged with sodium 4-methoxybenzenesulfinate (2e, 38.8 mg, 0.2 mmol), sodium 4-(trifluoromethyl)benzenesulfinate (2i, 46.4 mg, 0.2 mmol), KI (33.3 mg, 0.2 mmol), 2-methylquinoline (1a, 27 μL, 0.2 mmol), acetic acid (0.8 mL) and DMSO (0.8 mL) under air. Finally TBHP (30 μL, 0.2 mmol) was slowly added to the reaction vessel by syringe. The resulting solution was stirred at 80 °C for 3 h, and C-H sulfenylation products 3e and 3i were determined by GC in ratio 1:2.5.

**General procedure: (3a):**

A 10 mL oven-dried reaction vessel was charged with sodium benzenesulfinate (2a, 205 mg, 1.25 mmol), KI (83.3 mg, 0.5 mmol), 2-methylquinoline (1a, 67.5 μL, 0.5 mmol), acetic acid (0.8 mL) and DMSO (0.8 mL) under air. Finally TBHP (75 μL, 0.5 mmol) was slowly added to the reaction vessel by syringe. The resulting solution was stirred at 80 °C for 16 h. The volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3a as white solid; yield: 129.8 mg (92%), mp 122-124 °C.

2-((Phenylsulfonyl)methyl)quinoline (3a, CAS: 65492-27-5)[1]

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): δ 8.17 (d, $J = 8.4$ Hz, 1H), 7.83-7.81 (m, 2H), 7.68-7.66 (m, 3H), 7.60-7.53 (m, 3H), 7.43-7.39 (m, 2H), 4.74 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 149.2, 147.7, 138.3, 136.7, 133.7, 129.7, 129.1, 128.8, 128.4, 127.5, 127.2, 127.0, 122.6, 65.2.
2-((Tosylmethyl)quinoline (3b, CAS: 69722-31-2)[2]

\[
\begin{array}{c}
\text{O} \\
\text{S}
\end{array}
\]

The reaction was conducted with sodium 4-methylbenzenesulfinate (2b, 222.5 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3b as red solid; yield: 148 mg (90%), mp 161.1-162.5 °C.

\[ ^1\text{H NMR (CDCl}_3, 400 MHz, ppm): \delta \ 8.17 \ (d, J = 8.2 \ Hz, 1H), 7.88-7.81 \ (m, 2H), 7.68 \ (t, J = 7.5 \ Hz, 1H), 7.60-7.55 \ (m, 4H), 7.21 \ (d, J = 7.4 \ Hz, 2H), 4.72 \ (s, 2H), 2.39 \ (s, 3H); \ ^{13}\text{C NMR (100 MHz, CDCl}_3, ppm): \delta \ 149.3, 147.7, 144.6, 136.6, 135.4, 129.6, 129.4, 129.0, 128.3, 127.4, 127.2, 126.9, 122.5, 65.2, 21.4. \]

2-(((4-iso-Propylphenyl)sulfonyl)methyl)quinoline (3c)

\[
\begin{array}{c}
\text{O} \\
\text{S}
\end{array}
\]

The reaction was conducted with sodium 4-iso-propylbenzenesulfinate (2c, 257 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3c as yellow solid; yield: 124 mg (76%), mp 106.4-107.2 °C.

\[ ^1\text{H NMR (CDCl}_3, 400 MHz, ppm): \delta \ 8.16 \ (d, J = 8.4 \ Hz, 1H), 7.81 \ (d, J = 8.4 \ Hz, 2H), 7.65 \ (t, J = 7.6 \ Hz, 1H), 7.60-7.52 \ (m, 4H), 7.23 \ (d, J = 8.0 \ Hz, 2H), 4.72 \ (s, 2H), 2.95-2.88 \ (m, 1H), 1.22-1.20 \ (m, 6H); \ ^{13}\text{C NMR (CDCl}_3, 100 MHz, ppm): \delta \ 155.4, 149.4, 147.8, 136.7, 135.5, 129.7, 129.1, 128.6, 127.5, 127.3, 127.0, 126.9, 122.7, 65.3, 34.2, 23.5; \ \text{HRMS calcd. for: C}_{19}\text{H}_{19}\text{NO}_2\text{SNa [M+Na]^+} 348.1028, \text{found} 348.1022. \]

2-(((4-(tert-Butyl)phenyl)sulfonyl)methyl)quinoline (3d)
The reaction was conducted with sodium 4-(tert-butyl)benzenesulfinate (2d, 275 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3d as red solid; yield: 115.7 mg (68%), mp 151.2-153.4 °C. 

\( ^1H \) NMR (CDCl₃, 400 MHz, ppm): \( \delta \) 8.17 (d, \( J = 8.4 \) Hz, 1H), 7.81 (t, \( J = 8.3 \) Hz, 2H), 7.68-7.53 (m, 5H), 7.39 (d, \( J = 8.4 \) Hz, 2H), 4.72 (s, 2H), 1.29 (s, 9H); \( ^{13}C \) NMR (100 MHz, CDCl₃, ppm): \( \delta \) 157.6, 149.4, 147.8, 136.7, 135.2, 129.6, 129.1, 128.3, 127.5, 127.2, 127.0, 125.8, 122.7, 65.3, 35.1, 30.9; HRMS calcd. for: C₂₀H₂₁NO₂SNa [M+Na]⁺ 362.1185, found 362.1179.

2-(((4-Methoxyphenyl)sulfonyl)methyl)quinoline (3e)

The reaction was conducted with sodium 4-methoxybenzenesulfinate (2e, 242.5 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3e as yellow solid; yield: 142 mg (90%), mp 149.1-150.8 °C.

\( ^1H \) NMR (CDCl₃, 400 MHz, ppm): \( \delta \) 8.17 (d, \( J = 8.4 \) Hz, 1H), 7.88 (d, \( J = 8.5 \) Hz, 1H), 7.82 (d, \( J = 8.0 \) Hz, 1H), 7.70-7.66 (m, 1H), 7.60-7.53 (m, 4H), 6.87-6.83 (m, 2H), 4.72 (s, 2H), 3.81 (s, 3H); \( ^{13}C \) NMR (CDCl₃, 100 MHz, ppm): \( \delta \) 163.8, 149.5, 147.7, 136.9, 130.7, 129.8, 129.8, 129.1, 127.5, 127.3, 127.1, 122.7, 114.1, 65.4, 55.6; HRMS calcd. for: C₁₇H₁₅NO₃SNa [M+Na]⁺ 336.0664, found 336.0661.

2-(((4-Fluorophenyl)sulfonyl)methyl)quinoline (3f)

The reaction was conducted with sodium 4-fluorobenzenesulfinate (2f, 275 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3f as yellow solid; yield: 134 mg (86%), mp 150.0-152.2 °C.

\( ^1H \) NMR (CDCl₃, 400 MHz, ppm): \( \delta \) 8.17 (d, \( J = 8.4 \) Hz, 1H), 7.81 (t, \( J = 8.3 \) Hz, 2H), 7.68-7.53 (m, 5H), 7.39 (d, \( J = 8.4 \) Hz, 2H), 4.72 (s, 2H); \( ^{13}C \) NMR (100 MHz, CDCl₃, ppm): \( \delta \) 157.6, 149.4, 147.8, 136.7, 135.2, 129.6, 129.1, 128.3, 127.5, 127.2, 127.0, 125.8, 122.7, 65.3, 35.1, 30.9; HRMS calcd. for: C₂₀H₂₁NO₂SNa [M+Na]⁺ 362.1185, found 362.1179.

2-((4-Methoxyphenyl)sulfonyl)methyl)quinoline (3e)

The reaction was conducted with sodium 4-methoxybenzenesulfinate (2e, 242.5 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3e as yellow solid; yield: 142 mg (90%), mp 149.1-150.8 °C.

\( ^1H \) NMR (CDCl₃, 400 MHz, ppm): \( \delta \) 8.17 (d, \( J = 8.4 \) Hz, 1H), 7.88 (d, \( J = 8.5 \) Hz, 1H), 7.82 (d, \( J = 8.0 \) Hz, 1H), 7.70-7.66 (m, 1H), 7.60-7.53 (m, 4H), 6.87-6.83 (m, 2H), 4.72 (s, 2H), 3.81 (s, 3H); \( ^{13}C \) NMR (CDCl₃, 100 MHz, ppm): \( \delta \) 163.8, 149.5, 147.7, 136.9, 130.7, 129.8, 129.8, 129.1, 127.5, 127.3, 127.1, 122.7, 114.1, 65.4, 55.6; HRMS calcd. for: C₁₇H₁₅NO₃SNa [M+Na]⁺ 336.0664, found 336.0661.
The reaction was conducted with sodium 4-fluorobenzenesulfinate (2f, 227.5 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 µL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3f as yellow solid; yield: 100.1 mg (62%), mp 125.8-128.1 °C.

\[ ^1H \text{NMR (CDCl}_3, 400 \text{ MHz, ppm): } \delta 8.19 (d, J = 8.2 \text{ Hz, 1H}), 7.83-7.81 (m, 2H), 7.70-7.55 (m, 5H), 7.07 (t, J = 8.4 \text{ Hz, 2H}), 4.74 (s, 2H); \]
\[ ^{13}C \text{NMR (100 MHz, CDCl}_3, \text{ppm): } \delta 166.9 (J = 255 \text{ Hz}), 149.3, 147.9, 136.9, 131.5, 131.4, 130.0, 129.2, 127.6, 127.4, 127.2, 122.7, 116.1 (J = 22.6 \text{ Hz}), 65.4; \]
HRMS calcd. for: C_{16}H_{13}FNO_{2}S \ [M+H]^+ 302.0645, found 302.0646.

**2-(((4-Chlorophenyl)sulfonyl)methyl)quinoline (3g)**

The reaction was conducted with sodium 4-chlorobenzenesulfinate (2g, 247.5 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 µL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3g as white solid; yield: 112 mg (71%), mp 147.8-148.9 °C.

\[ ^1H \text{NMR (CDCl}_3, 400 \text{ MHz, ppm): } \delta 8.19 (d, J = 8.4 \text{ Hz, 1H}), 7.83 (d, J = 8.3 \text{ Hz, 2H}), 7.37 (d, J = 8.2 \text{ Hz, 2H}), 4.73 (s, 2H); \]
\[ ^{13}C \text{NMR (100 MHz, CDCl}_3, \text{ppm): } \delta 149.1, 147.9, 140.5, 137.0, 130.1, 130.0, 130.0, 129.2, 129.2, 127.6, 127.4, 127.3, 122.7, 65.3. \]

**2-(((4-Bromophenyl)sulfonyl)methyl)quinoline (3h)**

The reaction was conducted with sodium 4-bromobenzenesulfinate (2h, 302.5 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 µL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3h as white solid; yield: 130 mg (72%), mp 134.8-135.9 °C.

\[ ^1H \text{NMR (CDCl}_3, 400 \text{ MHz, ppm): } \delta 8.19 (d, J = 8.4 \text{ Hz, 1H}), 7.83 (d, J = 8.3 \text{ Hz, 2H}), 7.70 (t, J
= 7.6 Hz, 1H), 7.60-7.48 (m, 6H), 4.72 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 149.1, 147.9, 137.5, 137.0, 132.2, 130.1, 130.0, 129.2, 129.1, 127.6, 127.4, 127.3, 122.7, 65.3. HRMS calcd. for: C$_{16}$H$_{13}$BrNO$_2$S [M+H]$^+$ 361.9844, found 361.9842.

2-(((4-(Trifluoromethyl)phenyl)sulfonyl)methyl)quinoline (3i)

The reaction was conducted with sodium 4-(trifluoromethyl)benzenesulfinic acid (2i, 290 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3i as white solid; yield: 82.5 mg (47%), mp 180.5-181.4 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.21 (d, $J = 8.4$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.75 (t, $J = 9.6$ Hz, 3H), 7.70-7.65 (m, 3H), 7.62-7.55 (m, 2H), 4.76 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 148.8, 147.8, 141.7, 137.1, 135.4 (q, $J = 73.0$ Hz), 130.1, 129.3, 129.0, 127.6, 127.4, 127.3, 123.1 (q, $J = 271.0$ Hz), 125.9 (q, $J = 36.9$ Hz), 122.6, 65.1; HRMS calcd. for: C$_{17}$H$_{13}$F$_3$NO$_2$S [M+H]$^+$ 352.0613, found 352.0611.

2-(((4-(Trifluoromethoxy)phenyl)sulfonyl)methyl)quinoline (3j)

The reaction was conducted with sodium 4-(trifluoromethoxy)benzenesulfinic acid (2j, 310 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3j as dark solid; yield: 130 mg (71%), mp 141.8-143.2 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.20 (d, $J = 8.4$ Hz, 1H), 7.84-7.54 (m, 7H), 7.21 (d, $J = 8.2$ Hz, 2H), 4.74 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 153.0, 149.1, 147.8, 137.0, 136.5, 130.9, 130.0, 129.1, 127.5, 127.3, 127.26, 120.2 (q, $J = 258$ Hz), 122.6, 120.6, 65.3; HRMS calcd. for: C$_{17}$H$_{13}$F$_3$NO$_3$S [M+H]$^+$ 368.0562, found 368.0561.
2-((Naphthalen-2-ylsulfonyl)methyl)quinoline (3k)

The reaction was conducted with sodium naphthalene-2-sulfinate (2k, 267.5 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3k as yellow solid; yield: 85 mg (51%), mp 170.1-171.6 °C.

$^1$H NMR (CDCl₃, 400 MHz, ppm): $\delta$ 8.29 (s, 1H), 8.17 (d, $J = 8.4$ Hz, 1H), 7.89-7.80 (m, 4H), 7.74 (d, $J = 8.4$ Hz, 1H), 7.66-7.51 (m, 6H), 4.81 (s, 2H); $^{13}$C NMR (100 MHz, CDCl₃, ppm): $\delta$ 149.4, 147.9, 136.8, 135.6, 135.4, 132.1, 130.5, 129.8, 129.4, 129.2, 129.18, 129.1, 127.9, 127.5, 127.4, 127.4, 127.1, 123.1, 122.7, 65.4; HRMS calcd. for: C$_{20}$H$_{15}$NO$_2$SNa $\left[M+Na\right]^+$ 356.0715, found 356.0714.

2-((Methylsulfonyl)methyl)quinoline (3l, CAS: 19499-11-7)

The reaction was conducted with sodium methanesulfinate (2l, 127.5 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) to give 3l as yellow solid; yield: 55 mg (50%), mp 187.8-191.5 °C.

$^1$H NMR (CDCl₃, 400 MHz, ppm): $\delta$ 8.24 (d, $J = 8.4$ Hz, 1H), 8.07 (d, $J = 8.4$ Hz, 1H), 7.87 (s, 1H), 7.77 (t, $J = 7.5$ Hz, 1H), 7.62-7.59 (m, 2H), 4.61 (s, 2H), 2.96 (s, 3H); $^{13}$C NMR (100 MHz, CDCl₃, ppm): $\delta$ 150.0, 148.0, 137.4, 130.1, 129.2, 127.7, 127.5, 127.3, 122.8, 63.7, 40.1.

2-((Cyclopropylsulfonyl)methyl)quinoline (3m)

The reaction was conducted with sodium cyclopropanesulfinate (2m, 160 mg, 1.25 mmol) and 2-methylquinoline (1a, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography
(silica gel, petroleum ether/ethyl acetate = 7:1) to give 3m as yellow solid; yield: 69 mg (56%), mp 118-120 °C

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.22 (d, $J = 8.4$ Hz, 1H), 8.08 (d, $J = 8.4$ Hz, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.75 (t, $J = 7.6$ Hz, 1H), 7.66-7.57 (m, 2H), 4.68 (s, 2H), 2.47-2.40 (m, 1H), 1.13-1.10 (m, 2H), 0.97-0.94 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 149.9, 147.9, 137.0, 130.0, 129.2, 127.6, 127.4, 127.1, 122.7, 63.0, 29.3, 4.9; HRMS calcd. for: C$_{13}$H$_{14}$NO$_2$S $[M+H]^+$ 248.0739, found 248.0739.

6-Methyl-2-((phenylsulfonyl)methyl)quinoline (3n)

The reaction was conducted with sodium benzenesulfinate (2a, 205 mg, 1.25 mmol) and 2,6-dimethylquinoline (1b, 78.5 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3n as white solid; yield: 127.7 mg (86%), mp 132.5-133.7 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.07 (d, $J = 8.4$ Hz, 1H), 7.72-7.64 (m, 3H), 7.57-7.48 (m, 4H), 7.40 (t, $J = 7.6$ Hz, 2H), 4.71 (s, 2H), 2.53 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 148.2, 146.4, 138.3, 137.1, 136.1, 133.6, 132.1, 128.8, 128.79, 128.5, 127.3, 126.3, 122.6, 65.2, 21.5; HRMS calcd. for: C$_{17}$H$_{15}$NO$_2$SNa $[M+Na]^+$ 320.0715, found 320.0713.

6-Fluoro-2-((phenylsulfonyl)methyl)quinoline (3o)

The reaction was conducted with sodium benzenesulfinate (2a, 205 mg, 1.25 mmol) and 6-fluoro-2-methylquinoline (1c, 80.5 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) to give 3o as white solid; yield: 112.8 mg (75%), mp 161-162.5 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.13 (d, $J = 8.4$ Hz, 1H), 7.83 (m, 1H), 7.67 (d, $J = 7.6$ Hz,
2H), 7.59 (m, 2H), 7.43 (m, 4H), 4.72 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 160.7 (d, $J = 248$ Hz), 148.5, 144.9, 138.1, 136.2, 133.8, 131.6 (d, $J = 9.3$ Hz), 128.9, 128.4, 127.9 (d, $J = 10.4$ Hz), 123.4, 120.1 (d, $J = 25.8$ Hz), 110.5 (d, $J = 21.7$ Hz), 65.0; HRMS calcd. for: C$_{16}$H$_{12}$FNO$_2$SNa [M+Na]$^+$ 324.0465, found 324.0463.

**6-Bromo-2-((phenylsulfonyl)methyl)quinoline (3p)**

![Image of 6-Bromo-2-((phenylsulfonyl)methyl)quinoline (3p)](image)

The reaction was conducted with sodium benzenesulfinate (2a, 205 mg, 1.25 mmol) and 6-bromo-2-methylquinoline (1d, 111 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3p as yellow solid; yield: 157 mg (84%), mp 164.3-166.5 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.08 (d, $J = 8.4$ Hz, 1H), 7.98 (s, 1H), 7.74-7.65 (m, 4H), 7.61-7.56 (m, 2H), 7.42 (t, $J = 7.6$ Hz, 2H), 4.71 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 149.7, 146.3, 138.2, 135.7, 133.7, 133.2, 130.8, 129.5, 128.9, 128.4, 128.3, 123.5, 121.0, 65.1; HRMS calcd. for: C$_{16}$H$_{13}$BrNO$_2$S [M+H]$^+$ 361.9844, found 361.9841.

**7-Fluoro-2-((phenylsulfonyl)methyl)quinoline (3q)**

![Image of 7-Fluoro-2-((phenylsulfonyl)methyl)quinoline (3q)](image)

The reaction was conducted with sodium benzenesulfinate (2a, 205 mg, 1.25 mmol) and 7-fluoro-2-methylquinoline (1e, 80.5 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) to give 3q as yellow solid; yield: 141.5 mg (94%), mp 141.9-142.8 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.17 (d, $J = 8.4$ Hz, 1H), 7.84-7.80 (m, 1H), 7.67 (d, $J = 7.8$ Hz, 2H), 7.61-7.56 (m, 2H), 7.46-7.41 (m, 3H), 7.34 (t, $J = 7.5$ Hz, 1H), 4.72 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 163.1 (d, $J = 269.3$ Hz), 150.3, 148.6 (d, $J = 12.6$ Hz), 138.2, 136.6, 133.7, 129.5 (d, $J = 9.9$ Hz), 128.8, 128.3, 124.2, 122.0 (d, $J = 2.4$ Hz), 117.6 (d, $J = 25.4$ Hz), 112.6 (d, $J = 20.3$ Hz), 64.9; HRMS calcd. for: C$_{16}$H$_{13}$FNO$_2$S [M+H]$^+$ 302.0645, found 302.0645.
7-Chloro-2-((phenylsulfonyl)methyl)quinoline (3r)

The reaction was conducted with sodium benzenesulfinate (2a, 205 mg, 1.25 mmol) and 7-chloro-2-methylquinoline (1f, 89 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) to give 3r as white solid; yield: 143 mg (90%), mp 135.6-136.8 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.15 (d, $J = 8.4$ Hz, 1H), 7.83 (s, 1H), 7.76 (d, $J = 8.7$ Hz, 1H), 7.68 (d, $J = 7.6$ Hz, 2H), 7.62-7.58 (m, 2H), 7.51-7.49 (m, 1H), 7.43 (t, $J = 7.7$ Hz, 2H), 4.72 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 150.3, 148.0, 138.2, 136.5, 135.5, 133.7, 128.9, 128.7, 128.3, 128.0, 125.5, 122.8, 65.0; HRMS calcd. for: C$_{16}$H$_{13}$ClNO$_2$S [M+H]$^+$ 318.0350, found 318.0349.

8-Methoxy-2-((phenylsulfonyl)methyl)quinoline (3s)

The reaction was conducted with sodium benzenesulfinate (2a, 205 mg, 1.25 mmol) and 8-methoxy-2-methylquinoline (1g, 86.5 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 4:1) to give 3s as white solid; yield: 144 mg (92%), mp 142-143 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.13 (d, $J = 8.4$ Hz, 1H), 7.71 (d, $J = 7.4$ Hz, 2H), 7.63-7.55 (m, 2H), 7.48-7.37 (m, 4H), 7.02 (d, $J = 7.6$ Hz, 1H), 4.84 (s, 2H), 3.96 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 155.2, 147.9, 139.8, 138.4, 136.8, 133.6, 128.9, 128.5, 128.48, 127.3, 123.1, 119.3, 108.3, 65.1, 56.0; HRMS calcd. for: C$_{17}$H$_{15}$NO$_3$SNa [M+Na]$^+$ 336.0664, found 336.0660.

2-((Phenylsulfonfyl)methyl)quinolin-8-ol (3t)
The reaction was conducted with sodium benzenesulfinate (2a, 205 mg, 1.25 mmol) and 2-methylquinolin-8-ol (1h, 79.5 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give 3t as yellow solid; yield: 113.6 mg (76%), mp 157.6-159.8 °C.

\[ \text{1H NMR (CDCl}_3, 400 MHz, ppm): } \delta \text{ 8.17 (d, } J = 8.4 \text{ Hz, 1H), 7.66-7.56 (m, 4H), 7.47-7.32 (m, 5H), 7.11 (d, } J = 7.5 \text{ Hz, 1H), 4.71 (s, 2H); } \text{13C NMR (CDCl}_3, 100 MHz, ppm): } \delta \text{ 151.8, 147.2, 138.2, 137.6, 137.2, 133.9, 128.9, 128.5, 128.45, 127.6, 123.5, 117.7, 110.5, 64.7; HRMS calcd. for: C}_{16}H_{13}NO_{3}SNa [M+Na]^+ 322.0508, found 322.0507. \]

2-Methyl-3-((phenylsulfonyl)methyl)quinoxaline (3u)

The reaction was conducted with sodium benzenesulfinate (2a, 205 mg, 1.25 mmol) and 2,3-dimethylquinoxaline (1i, 79 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3u as white solid; yield: 74.6 mg (50%), mp 199-201 °C.

\[ \text{1H NMR (CDCl}_3, 400 MHz, ppm): } \delta \text{ 8.01 (d, } J = 8.2 \text{ Hz, 1H), 7.74-7.62 (m, 6H), 7.50-7.44 (m, 2H), 4.82 (s, 2H), 2.89 (s, 3H); } \text{13C NMR (CDCl}_3, 100 MHz, ppm): } \delta \text{ 154.1, 144.3, 141.6, 140.7, 138.1, 134.0, 130.6, 129.4, 129.1, 128.8, 128.7, 128.4, 62.1, 23.1. HRMS calcd. for: C}_{16}H_{14}N_{2}O_{2}SNa [M+Na]^+ 321.0614, found 326.0611. \]

2-Phenyl-3-((phenylsulfonyl)methyl)quinoxaline (3v)

The reaction was conducted with sodium benzenesulfinate (2a, 205 mg, 1.25 mmol) and 2-methyl-3-phenylquinoxaline (1j, 110 mg, 0.5 mmol). The residue was purified by column
chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3v as white solid; yield: 124.2 mg (69%), mp 140-142 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): δ 8.13 (d, $J = 7.8$ Hz, 1H), 7.88 (d, $J = 7.8$ Hz, 1H), 7.78 (m, 2H), 7.62 (m, 5H), 7.47 (m, 5H), 4.91 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): δ 155.4, 143.4, 141.3, 140.9, 138.9, 137.5, 133.8, 131.0, 130.3, 129.2, 129.2, 129.0, 128.9, 128.7, 128.6, 61.1. HRMS calcd. for: C$_{21}$H$_{16}$N$_2$O$_2$SNa [M+Na]$^+$ 383.0825, found 383.0827.

6-Fluoro-4-(phenylsulfonyl)-2-((phenylsulfonyl)methyl)quinoline (3w)

![Chemical structure of 3w](image)

The reaction was conducted with sodium benzenesulfinate (2a, 205 mg, 1.25 mmol) and 4-chloro-6-fluoro-2-methylquinoline (1k, 97.5 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) to give 3w as yellow solid; yield: 163 mg (37%), mp 173-175 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): δ 8.32-8.28 (m, 2H), 8.02-7.96 (m, 3H), 7.71-7.44 (m, 9H), 4.79 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): δ 161.8 (d, $J = 252$ Hz), 148.4, 146.4, 145.3, 139.7, 138.2, 134.3, 134.2, 133.2, 133.1, 123.5, 129.7, 129.3, 128.4, 128.1, 123.9, 121.3 (d, $J = 26$ Hz), 108.4 (d, $J = 26$ Hz), 64.8; HRMS calcd. for: C$_{22}$H$_{16}$ClFNO$_2$S$_2$Na [M+Na]$^+$ 464.0397, found 464.0396.

References:


$^1$H and $^{13}$C NMR spectra of products