

Supporting Information

Transition-Metal-Free Desulfinative Cross-Coupling of Heteroaryl Sulfinates with Grignard Reagents

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Table of Contents

1. General information	S3
2. Typical procedure for the synthesis of 1a-1p	S3-S4
3. Characterization data of 1a-1p	S5-10
4. General procedure for the synthesis of Grignard reagents 1f-1o	S10
5. General procedure for the synthesis of 3aa-3oa, 3ab-3al, 3lb, 3le, 3lm, 3ln, 3ob, 3oc, 3oo-3or	S10-S11
6. Characterization data of 3aa-3oa, 3ab-3al, 3lb, 3le, 3lm, 3ln, 3ob, 3oc, 3oo-3or	S11-S24
7. ICP-OES analysis	S24
8. Mechanistic studies	
1) Preparation of LiDBB	S25
2) Effect of Single Electron Donors (LiDBB)	S25
3) Radical trapping experiments	S25
4) Radical clock reaction	S26
5) Competition experiments of <i>p</i> -Me ₂ NC ₆ H ₄ MgBr and <i>p</i> -CF ₃ C ₆ H ₄ MgBr	S26
6) Reaction of sulfonate with Arylzinc reagents and PhLi	S26
7) The proposed mechanism and the fate of the leaving group	S26
9. Scale-up experiment	S27
10. Copies of NMR Spectra	S28-87

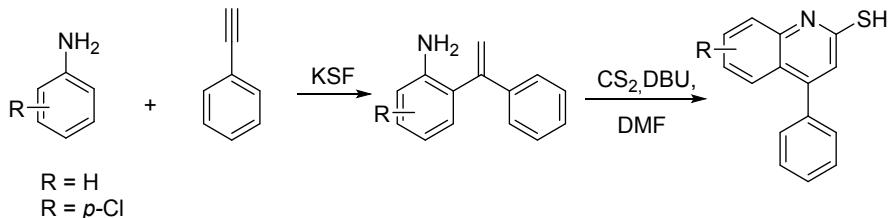
1. General information

Unless otherwise mentioned, all manipulations were conducted with a standard Schlenk tube under N₂ atmosphere, and reagents were purchased from commercial sources and used without further purification. Dry THF was freshly distilled over sodium with the use of diphenyl ketone as an indicator. Flash chromatography was performed using 300-400 mesh silica gel. NMR spectra were obtained on a Bruker AV400 or Agilent MR400 (400 MHz for ¹H; 376 MHz for ¹⁹F; 100 MHz for ¹³C). ¹H NMR and ¹³C NMR chemical shifts were determined relative to internal (CH₃)₄Si (TMS) at δ 0.0. All the melting points were uncorrected. Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the ESI mode. ICP-OES analysis was performed using a Leeman Prodigy ICP spectrometer.

PhMgBr **2a** (2.0 M in THF), *p*-CH₃PhMgBr **2b** (1.0 M in THF), *o*-CH₃PhMgBr **2c** (1.0 M in THF), *m*-CH₃PhMgBr **2d** (1.0 M in THF), *p*-OCH₃PhMgBr **2e** (1.0 M in THF), MeMgBr **2p** (1.0 M in THF), Cyclopropylmagnesium bromide **2q** (1.0 M in THF), Vinylmagnesium bromide **2r** (1.0 M in THF), ethynylmagnesium bromide **2s** (1.0 M in THF) were commercial available.

2. Typical procedure for the synthesis of 1a-1p

2.1 General procedure for the synthesis of 4-phenylquinoline-2-thiol

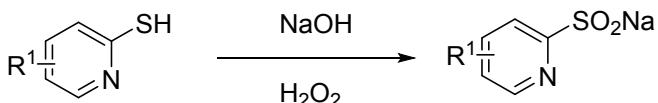


4-phenylquinoline-2-thiol was prepared according to the reported procedures. (Wang, T.-L.; Liu, X.-J.; Huo, C.-D.; Wang, X.-C.; Quan, Z.-J. *Chem. Commun.* **2018**, *54*, 499-502.) 5.0 g of montmorillonites K10 was added to a solution of phenylacetylene (5.1 g, 50.0 mmol) and para-tolylidine (50.0 mmol) in the xylene (25.0 mL). The mixture was heated at the 140 °C under stirring for 5 hours. After filtration, the volatiles were removed in vacuum. The residue was purified by column chromatography on silica gel (eluting with 100% petroleum ether) to give the corresponding products. (R = H, 75%; R = *p*-Cl, 54%)

Under an atmosphere of air, 2-(1-phenylvinyl)aniline (1.0 g, 5.1 mmol, 1.0 equiv), CS₂ (463.6 mg, 6.1 mmol, 1.2 equiv), DBU (40 μ L, 5 mol%) were added to a tube. DMF was added and stirred for 8 h at 140 °C. Then the mixture was poured into ice water and a yellow precipitate appeared, which was filtered and dried in vacuum for direct use without further purification. (R = H, 92%; R = *p*-Cl, 68%)

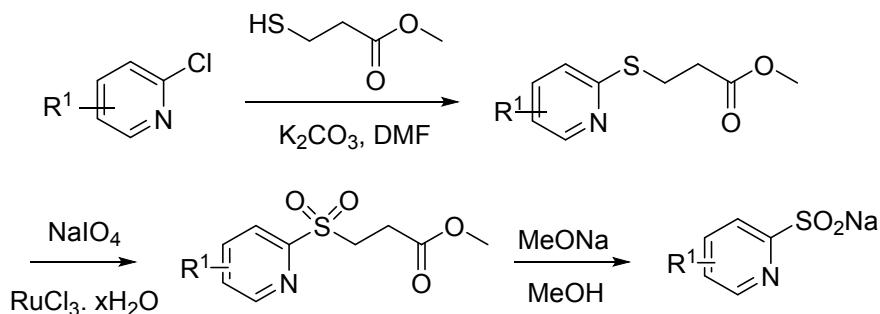
2.2 General procedure for the synthesis of heteroaryl sulfonates 1a-1p

General procedure A:



Modified procedure according to the reported procedures. (Markovic, T.; Rocke, B. N.; Blakemore, D. C.; Mascittib, V.; Willis, M. C. *Org. Lett.* **2017**, *19*, 6033–6035.) Heteroaryl thiol (1.0 equiv) was dissolved in a mixture of 20 mL of water containing sodium hydroxide (1.3 equiv) and 100 mL of ethanol. An aqueous solution of hydrogen peroxide (30% (w/w) in H₂O, 1.1 equiv) was added dropwise at room temperature and stirred until reaction complete. The solvent was removed under reduced pressure and the residue was washed with ethyl acetate (3 × 50 mL). The aqueous phase was evaporated to afford the crude product. Recrystallization from methanol and ethyl acetate to obtain corresponding purified sodium sulfinate.

General procedure B:

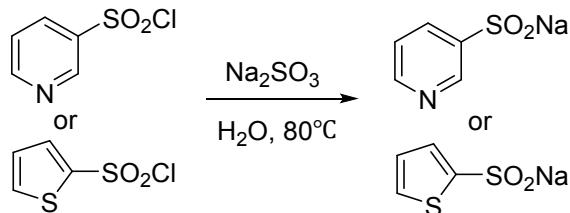


Methyl 3-mercaptopropanoate (2 mL, 17.6 mmol, 1.5 equiv) was added to a solution of 2-chloropyridine (11.7 mmol, 1.0 equiv) and K₂CO₃ (2.4 g, 17.6 mmol, 1.5 equiv) in DMF. The mixture was stirred at room temperature for 3 hours. Then the mixture was poured into ice water and a white precipitate appeared, which was filtered for direct use without further purification.

The crude sulfide (7.5 mmol) was dissolved in MeCN 15 mL, H₂O 30 mL, and DCM 15 mL, then NaIO₄ (2.5 equiv) and RuCl₃·xH₂O (10 mol%) was added. The mixture was stirred at room temperature for five hours. The reaction was quenched with saturated NaHCO₃ and extracted with DCM. The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. Purification by column chromatography (eluting with petroleum ether/ethyl acetate = 3/1) yielded the sulfone derivative as a white solid.

To a solution of the corresponding sulfone derivative (5.0 mmol) in MeOH was added NaOMe (1 mL, 1.0 equiv, 5 M in MeOH) in drop wise. After stirring for 30 minutes at room temperature, the solvent was removed under reduced pressure to get a residue, which was recrystallized with methanol to furnish the corresponding sulfinate salts.

General procedure C:

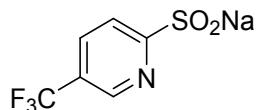


Sodium pyridine-3-sulfinate **1j** (or sodium thiophene-2-sulfinate **1o**) was prepared by heating 2.5 g of sodium sulfite, 1.7 g of pyridine-3-sulfonyl chloride (or 1.8 g thiophene-2-sulfonyl chloride) and 1.68 g of sodium bicarbonate in 10.0 mL of water at 80 °C for 4 h. After

cooling to room temperature, water was removed under vacuum to get a residue, which was recrystallized with ethanol to get target compound **1j** with a yield of 84% (**1o**, 79%).

3. Characterization data of **1a-1p**

sodium 5-(trifluoromethyl)pyridine-2-sulfinate (1a)



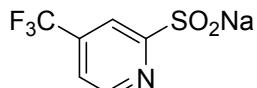
General procedure **A** was followed using 5-(trifluoromethyl)pyridine-2-thiol (5.0 g, 27.9 mmol). Product **1a** was obtained as a white solid (5.8 g, 89%). ¹H NMR (400 MHz, D₂O) δ 8.72 (s, 1H), 8.18 (dd, *J*=8.4 Hz, 2.0 Hz, 1H), 7.82 (d, *J*= 8.4 Hz, 1H). ¹⁹F NMR (376 MHz, D₂O) δ -62.53. ¹³C NMR (100 MHz, D₂O) δ 174.2, 146.0 (q, *J*= 5.0 Hz), 136.7 (q, *J*= 3.0 Hz), 127.9 (q, *J*= 33.3 Hz), 127.2 (q, *J*= 272.7 Hz), 117.5. HRMS (ESI): m/z calcd. for C₆H₃F₃NO₂S [M-Na+2H]⁺ 211.9988, found 211.9983. (Markovic, T.; Rocke, B. N.; Blakemore, D. C.; Mascittib, V.; Willis, M. C. *Org. Lett.* **2017**, *19*, 6033–6035.)

sodium 3-chloro-5-(trifluoromethyl)pyridine-2-sulfinate (1b)



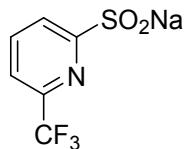
General procedure **A** was followed using 3-chloro-5-(trifluoromethyl)pyridine-2-thiol (2.13g, 10.0 mmol). Product **1b** was obtained as a white solid (1.8g, 67%). mp>300 °C; ¹H NMR (400 MHz, D₂O) δ 8.69 (s, 1H), 8.12 (s, 1H). ¹⁹F NMR (376 MHz, D₂O) δ -61.69. ¹³C NMR (100 MHz, D₂O) δ 168.1, 144.6 (q, *J*= 4.0 Hz), 136.8 (q, *J*= 3.0 Hz), 129.7, 128.9 (q, *J*= 34.3 Hz), 126.4 (q, *J*= 273.7 Hz). IR_ν_{max} (KBr)/cm⁻¹ 3030, 1588, 1428, 1382, 1319, 1144, 1041, 994, 920, 850, 726. HRMS (ESI): m/z calcd. For C₆H₂ClF₃NO₂S [M-Na+2H]⁺ 245.9598, found 245.9601.

sodium 4-(trifluoromethyl)pyridine-2-sulfinate (1c)



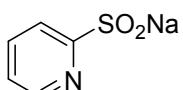
General procedure **A** was followed using 4-(trifluoromethyl)pyridine-2-thiol (1.0 g, 5.5 mmol). Product **1c** was obtained as a white solid (845.0 mg, 66%). ¹H NMR (400 MHz, D₂O) δ 8.60 (d, *J*= 5.2 Hz, 1H), 7.91, 7.62 (d, *J*= 4.4 Hz, 1H). ¹⁹F NMR (376 MHz, D₂O) δ -64.75. ¹³C NMR (100 MHz, D₂O) δ 172.3, 150.4, 140.6 (q, *J*= 34.3 Hz), 126.6 (q, *J*= 274.7 Hz), 121.2 (q, *J*= 3.0 Hz), 113.6 (q, *J*= 4.0 Hz). HRMS (ESI): m/z calcd. for C₆H₃F₃NO₂S [M-Na+2H]⁺ 211.9988, found 211.9983. (Markovic, T.; Rocke, B. N.; Blakemore, D. C.; Mascittib, V.; Willis, M. C. *Org. Lett.* **2017**, *19*, 6033–6035.)

sodium 6-(trifluoromethyl)pyridine-2-sulfinate (1d)



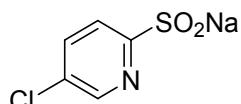
General procedure **B** was followed using 2-chloro-6-(trifluoromethyl)pyridine. Product **1d** was obtained as a white solid (64%, over three steps). mp 56–58 °C; ¹H NMR (400 MHz, D₂O) δ 8.05 (t, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H). ¹⁹F NMR (376 MHz, D₂O) δ –67.45. ¹³C NMR (100 MHz, D₂O) δ 171.9, 146.8 (q, *J* = 32.3 Hz), 141.0, 125.3 (q, *J* = 271.7 Hz), 122.2, 120.4. IR ν_{max} (KBr)/cm^{–1} 3063, 1705, 1586, 1134, 952, 826, 748. HRMS (ESI): m/z calcd. for C₆H₃F₃NO₂S [M-Na]⁺ 209.9837, found 209.9841.

sodium pyridine-4-sulfinate (1e)



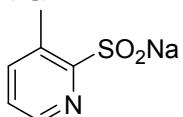
General procedure **A** was followed using pyridine-2-thiol (500 mg, 4.5 mmol). Product **1e** was obtained as a white solid (500.2 mg, 67%). ¹H NMR (400 MHz, D₂O) δ 8.49 (d, *J* = 5.2 Hz, 1H), 7.95 (qd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.40–7.37 (m, 1H). (Markovic, T.; Rocke, B. N.; Blakemore, D. C.; Mascittib, V.; Willis, M. C. *Org. Lett.* **2017**, *19*, 6033–6035.)

sodium 5-chloropyridine-2-sulfinate (1f)



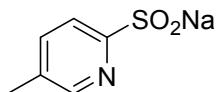
General procedure **A** was followed using 5-chloropyridine-2-thiol (1.0 g, 6.8 mmol). Product **1f** was obtained as a white solid (1.0 g, 74%). ¹H NMR (400 MHz, D₂O) δ 8.37 (d, *J* = 2.0 Hz, 1H), 7.88 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H). ¹³C NMR (100 MHz, D₂O) δ 168.8, 147.5, 138.8, 133.3, 118.5. (Markovic, T.; Rocke, B. N.; Blakemore, D. C.; Mascittib, V.; Willis, M. C. *Org. Lett.* **2017**, *19*, 6033–6035.)

sodium 3-methylpyridine-2-sulfinate (1g)



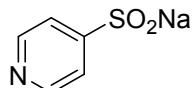
General procedure **A** was followed using 3-methylpyridine-2-thiol (1.25 g, 10 mmol). Product **1g** was obtained as a white solid (1.2 g, 70%). ¹H NMR (400 MHz, D₂O) δ 8.35 (s, 1H), 7.66–7.37 (m, 1H), 7.35 (s, 1H), 2.53 (s, 3H). (Markovic, T.; Rocke, B. N.; Blakemore, D. C.; Mascittib, V.; Willis, M. C. *Org. Lett.* **2017**, *19*, 6033–6035.)

sodium 5-methylpyridine-2-sulfinate (1h)



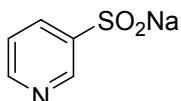
General procedure **A** was followed using 5-methylpyridine-2-thiol (1.25 g, 10 mmol). Product **1h** was obtained as a white solid (1.3 g, 75%). ¹H NMR (400 MHz, D₂O) δ 8.34 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 2.53 (s, 3H). (Markovic, T.; Rocke, B. N.; Blakemore, D. C.; Mascittib, V.; Willis, M. C. *Org. Lett.* **2017**, *19*, 6033–6035.)

sodium 5-methylpyridine-2-sulfinate (1i)



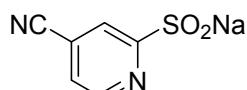
General procedure **A** was followed using 5-methylpyridine-2-thiol (1.1 g, 10 mmol). Product **1i** was obtained as a white solid (1.3 g, 80%). ¹H NMR (400 MHz, D₂O) δ 8.64 (dd, *J* = 4.4 Hz, 1.2 Hz, 2H), 7.62 (dd, *J* = 4.4 Hz, 1.6 Hz, 2H). (Markovic, T.; Rocke, B. N.; Blakemore, D. C.; Mascittib, V.; Willis, M. C. *Org. Lett.* **2017**, *19*, 6033–6035.)

sodium 3-methylpyridine-2-sulfinate (1j)



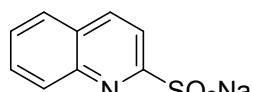
General procedure **C** was followed using pyridine-3-sulfonyl chloride (1.7 g, 10 mmol). Product **1j** was obtained as a white solid (1.3 g, 80%). ¹H NMR (400 MHz, D₂O) δ 8.52 (d, *J* = 2.0 Hz, 1H), 8.42 (dd, *J* = 4.8 Hz, 1.2 Hz, 1H), 7.88 (dt, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.40 (q, *J* = 4.8 Hz, 1H). (Markovic, T.; Rocke, B. N.; Blakemore, D. C.; Mascittib, V.; Willis, M. C. *Org. Lett.* **2017**, *19*, 6033–6035.)

sodium 4-cyanopyridine-2-sulfinate (1k)



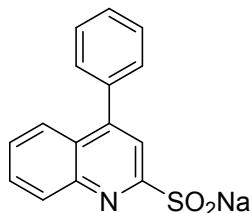
General procedure **B** was followed using 2-chloroisonicotinonitrile. Product **1k** was obtained as a white solid (58% over three steps). mp 233–234 °C; ¹H NMR (400 MHz, D₂O) δ 8.58 (d, *J* = 4.4 Hz, 1H), 8.03 (s, 1H), 7.70 (s, 1H). ¹³C NMR (100 MHz, D₂O) δ 171.4, 166.5, 149.5, 141.0, 122.4, 114.7. IR ν_{max} (KBr)/cm⁻¹ 2210, 1645, 1541, 1439, 1338, 1193, 1059, 988. HRMS (ESI): m/z calcd. for C₆H₃N₂O₂S [M-Na]⁻ 166.9915, found 166.9923.

sodium quinoline-2-sulfinate (1l)



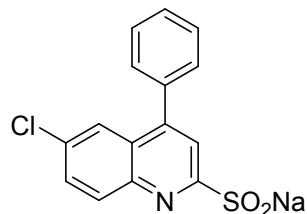
General procedure **A** was followed using quinoline-2-thiol (862 mg, 5.3 mmol). Product **1l** was obtained as a white solid (187 mg, 87%). ¹H NMR (400 MHz, D₂O) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H). ¹³C NMR (100 MHz, D₂O) δ 170.9, 145.4, 139.8, 130.7, 128.3, 128.1, 127.6, 127.3, 113.2. HRMS (ESI): m/z calcd. for C₉H₆NO₂S [M-Na]⁻ 192.0119, found 192.0117. (Markovic, T.; Rocke, B. N.; Blakemore, D. C.; Mascittib, V.; Willis, M. C. *Org. Lett.* **2017**, *19*, 6033–6035.)

2-sodium 4-phenylquinoline-2-sulfinate (1m)



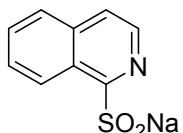
General procedure **A** was followed using 4-phenylquinoline-2-thiol (1.0 g, 4.2 mmol). Product **1m** was obtained as a white solid (904 mg, 74%). mp > 300 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.88–7.76 (m, 3H), 7.67–7.50 (m, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 177.3, 148.7, 147.3, 138.5, 130.0, 129.8, 129.7, 129.2, 128.9, 127.1, 126.3, 125.7, 115.5. IR_{max} (KBr)/cm⁻¹ 3091, 1582, 1061, 984, 765, 701. HRMS (ESI): m/z calcd. for C₁₅H₁₀NO₂S [M-Na]⁻ 268.0432, found 268.0435.

sodium 6-chloro-4-phenylquinoline-2-sulfinate (1n)



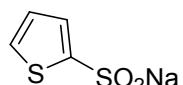
General procedure **A** was followed using 6-chloro-4-phenylquinoline-2-thiol (700 mg, 2.6 mmol). Product **1n** was obtained as a white solid (532 mg, 63%). mp > 300 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.11 (d, *J* = 8.8 Hz, 1H), 7.77 (s, 1H), 7.77–7.73 (dd, *J* = 9.2 Hz, 2.4 Hz, 1H), 7.69 (d, *J* = 2.4 Hz, 1H), 7.62–7.48 (m, 5H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 178.4, 147.9, 145.8, 137.9, 132.1, 131.5, 130.2, 129.6, 129.4, 129.2, 127.1, 124.3, 116.4. IR_{max} (KBr)/cm⁻¹ 1486, 1156, 1043, 969, 702, 654. HRMS (ESI): m/z calcd. for C₁₅H₉ClNO₂S [M-Na]⁻ 302.0042, found 302.0048.

sodium isoquinoline-1-sulfinate (1o)



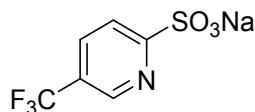
General procedure **A** was followed using isoquinoline-1-thiol (1.6 g, 10 mmol). Product **1o** was obtained as a white solid (1.4 g, 65%). ¹H NMR (400 MHz, D₂O) δ 8.73 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 5.6 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 6.0 Hz, 1H), 7.61–7.59 (m, 1H), 7.55–7.50 (m, 1H). (Markovic, T.; Rocke, B. N.; Blakemore, D. C.; Mascittib, V.; Willis, M. C. *Org. Lett.* **2017**, *19*, 6033–6035.)

sodium thiophene-2-sulfinate (1p)



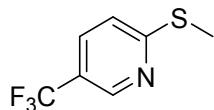
General procedure C was followed using thiophene-2-sulfonyl chloride (1.8 g, 10.0 mmol). Product **1p** was obtained as a white solid (1.3 g, 79%). ¹H NMR (400 MHz, D₂O) δ 7.61 (d, *J* = 4.8 Hz, 1H), 7.37 (d, *J* = 3.2 Hz, 1H), 7.15 (t, *J* = 4.4 Hz, 1H). ¹³C NMR (100 MHz, D₂O) δ 158.3, 128.5, 127.7, 126.5. (Meyer, A. U.; Straková, K.; Slanina, T.; König, B. *Chem. - Eur. J.* **2016**, 22, 8694 – 8699)

sodium 5-(trifluoromethyl)pyridine-2-sulfonate



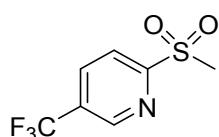
General procedure A was followed using 5-(trifluoromethyl)pyridine-2-thiol (1.8 g, 10 mmol), H₂O₂ (30% (w/w) in H₂O, 5 equiv). Product was obtained as a white solid (1.6 g, 65%). mp > 300 °C; ¹H NMR (400 MHz, D₂O) δ 8.79 (s, 1H), 8.21-8.19 (m, 1H), 7.96 (d, *J* = 8.0 Hz, 1H). ¹³C NMR (100 MHz, D₂O) δ 161.5, 146.5 (q, *J* = 3.0 Hz), 138.8 (q, *J* = 3.0 Hz), 128.7 (q, *J* = 33.0 Hz), 126.9 (q, *J* = 271.0 Hz), 121.1. ¹⁹F NMR (376 MHz, D₂O) δ -62.76. IR ν_{max} (KBr)/cm⁻¹ 1575, 1332, 1257, 1075, 1048, 845, 726, 656. HRMS (ESI): m/z calcd. for C₆H₃F₃NO₃S [M-Na]⁻ 225.9786, found 225.9784.

2-(methylthio)-5-(trifluoromethyl)pyridine



5-(Trifluoromethyl)pyridine-2-thiol (2.69 g, 15.0 mmol) was dissolved in THF (13.5 mL) and CH₃CN (1.5 mL) at 0 °C. DBU (2.51 g, 16.5 mmol) was added dropwise and the resulting reaction mixture was stirred for 20 min. Then, MeI (2.34 g, 16.5 mmol) was added, the ice bath was removed and the reaction mixture was stirred for 12 h. Addition of H₂O (50 mL) was followed by extraction using EtOAc (3 × 50 mL). Purification by flash chromatography (silica gel, pentane / ethyl acetate = 100:1) afforded the product (1.59 g, 55%) as a pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.65 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 2.57 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.21. (Metzger, A.; Melzig, L.; Despotopoulou, C.; Knochel, P. *Org. Lett.* **2009**, 11, 5228-4231.)

2-(methylsulfonyl)-5-(trifluoromethyl)pyridine



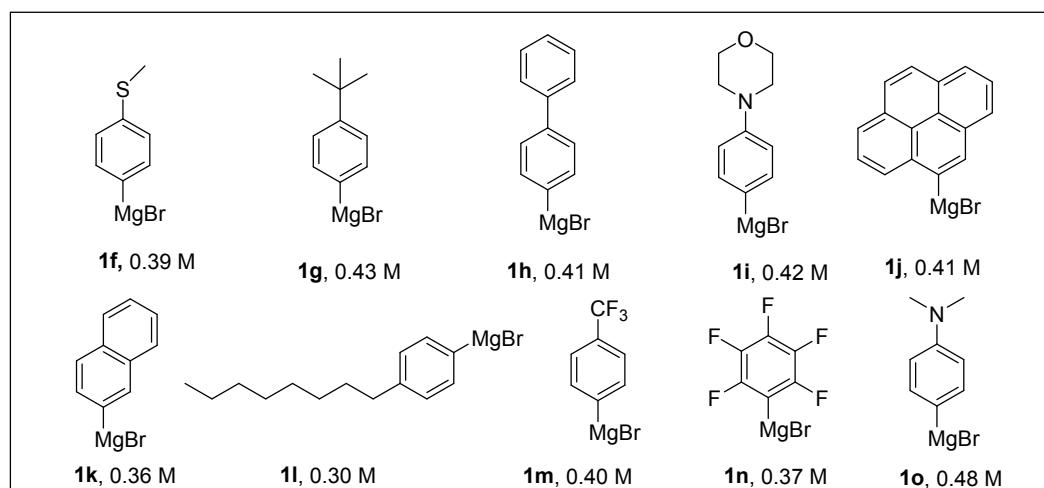
The 2-(methylthio)-5-(trifluoromethyl)pyridine (1.0 g, 5.2 mmol) was dissolved in MeCN 15 mL, H₂O 30 mL, and DCM 15 mL, then NaIO₄ (13 mmol, 2.5 equiv) and RuCl₃·xH₂O (10 mol%) was added. The mixture was stirred at room temperature for five hours. The reaction

was quenched with saturated NaHCO_3 and extracted with DCM. The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure. Purification by column chromatography (eluting with petroleum ether/ethyl acetate = 10/1) yielded the sulfone derivative as a white solid (1.1 g, 93%). ^1H NMR (400 MHz, CDCl_3) δ 8.98 (s, 1H), 8.24-8.24 (m, 2H), 3.28 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -62.72. HRMS (ESI): m/z calcd. for $\text{C}_6\text{H}_3\text{F}_3\text{NO}_3\text{S} [\text{M}+\text{H}]^+$ 226.0144, found 226.0142.

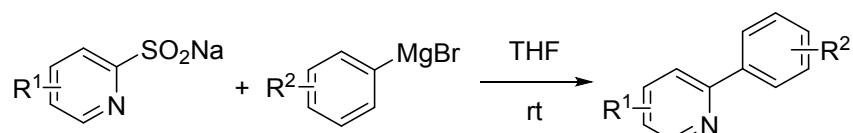
4. General procedure for the synthesis of Grignard reagents **1f-1o**.

An oven-dried 25-mL Schlenk round-bottom flask equipped with a reflux condenser and a stir bar was sealed and heated under vacuum for 2 minutes with the help of a heat gun. After cooling down, the Schlenk flask was back-filled with Ar. Mg turnings were added under a positive pressure of Ar. The Schlenk flask was then sealed, evacuated and back-filled with Ar (this process was repeated 3 times). A solution of the aryl bromide (2.0 mmol) in THF (6 mL) was added at room temperature. The reaction was initiated by gently heating the flask with a heat gun. Once the reaction had initiated, a solution of the aryl bromide (6.0 mmol) in THF (10 mL) was added dropwise over 10 minutes. The resulting mixture was stirred at 80 °C for 30 minutes and cool to room temperature.

The concentration of Grignard reagents were determined by iodometric titration. A solution of Grignard reagent was added dropwise to a stirred solution of iodine (51 mg, 0.2 mmol) in THF (1 mL) until decoloration. The volume of the solution needed for the titration was used to calculate the concentration of Grignard reagent. (Levin, V. V.; Zemtsov, A. A.; Struchkova, M. I.; Dilman, A. D. *Org. Lett.* **2013**, *15*, 917-919.)



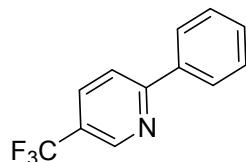
5. General procedure for the synthesis of **3aa-3oa**, **3ab-3al**, **3lb**, **3le**, **3lm**, **3ln**, **3ob**, **3oc**, **3oo-3or**



Under an atmosphere of N_2 , Grignard reagent (1.5 mmol, 1.5 equiv) was added to a solution of heteroaryl sulfinate (1.0 mmol, 1.0 equiv) in THF (3 mL). The mixture was stirred at room temperature for 12 hours. Addition of H_2O (5 mL) was followed by extraction using EtOAc (3×10 mL). Then the combined organic layers were removed under reduced pressure and the residue was purified by column chromatography to furnish the target product.

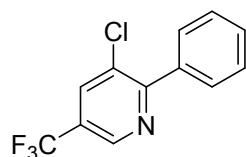
6. Characterization data of **3aa-3oa, 3ab-3al, 3lb, 3le, 3lm, 3ln, 3ob, 3oc, 3oo-3or**

2-phenyl-5-(trifluoromethyl)pyridine (3aa)



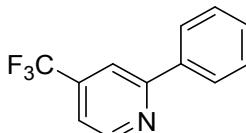
General procedure was followed using sodium 5-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3aa** as a white solid (194.0 mg, 87%). ^1H NMR (400 MHz, CDCl_3) δ 8.95 (s, 1H), 8.05–8.03 (m, 2H), 7.99 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.54–7.48 (m, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -62.3. ^{13}C NMR (100 MHz, CDCl_3) δ 160.7, 146.6 (q, J = 4.0 Hz), 138.0, 134.0 (q, J = 4.0 Hz), 130.1, 129.0, 128.7 (q, J = 270.0 Hz), 127.3, 125.3 (q, J = 33.0 Hz), 120.0. (Wang, Dan.; Chen, H.-G.; Tian, X.-C.; Liang, X.-X.; Chen, F.-Z.; Gao, Feng. *RSC Adv.* **2015**, 5, 107119-107122.)

3-chloro-2-phenyl-5-(trifluoromethyl)pyridine (3ba)



General procedure was followed using sodium 3-chloro-5-(trifluoromethyl)pyridine-2-sulfinate (267.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ba** as a white solid (190.0 mg, 74%). ^1H NMR (400 MHz, CDCl_3) δ 8.85 (s, 1H), 8.03 (s, 1H), 7.77–7.75 (m, 2H), 7.50–7.48 (m, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -62.2. ^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 144.3 (q, J = 4.0 Hz), 137.0, 135.3 (q, J = 4.0 Hz), 130.2, 129.7, 129.4, 128.2, 127.3, 126.8 (q, J = 271.0 Hz), 126.6 (q, J = 33.0 Hz), 119.0. (Zhou, Q.; Zhang, B.; Su, L.; Jiang, T.; Chen, R.; Du, T.; Ye, Y.; Shen, J.; Dai, G.; Han, D.; Jiang, H. *Tetrahedron* **2013**, 69, 10996-11003.)

2-phenyl-4-(trifluoromethyl)pyridine (3ca)



General procedure was followed using sodium 4-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel

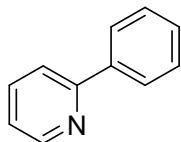
(eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ca** as a white solid (167.0 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ 8.85 (d, *J* = 4.8 Hz, 1H), 8.02 (d, *J* = 7.2 Hz, 2H), 7.91 (s, 1H), 7.51–7.42 (m, 4H). ¹⁹F NMR (376 MHz, CDCl₃) δ –64.9. ¹³C NMR (100 MHz, CDCl₃) δ 158.8, 150.6, 139.7 (q, *J* = 33.0 Hz), 138.0, 129.9, 129.0, 127.1, 124.3 (q, *J* = 270.0 Hz), 117.5 (d, *J* = 3.0 Hz), 116.1 (m). (Paterson, A. J.; Heron, C. J.; McMullin, C. L.; Mahon, M. F.; Pressc, N. J.; Frost, C. G. *Org. Biomol. Chem.* **2017**, *15*, 5993–6000.)

2-phenyl-6-(trifluoromethyl)pyridine (3da)



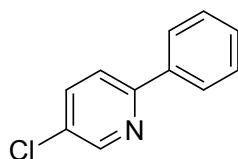
General procedure was followed using sodium 6-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 50/1) to afford product **3da** as a white solid (181.0 mg, 81%). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (m, 2H), 7.91 (d, *J* = 4.0 Hz, 2H), 7.63–7.58 (m, 1H), 7.53–7.44 (m, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ –68.1. ¹³C NMR (100 MHz, CDCl₃) δ 157.8, 148.7 (q, *J* = 35.0 Hz), 138.0, 137.8, 129.8, 128.9, 127.1, 125.7 (q, *J* = 270.0 Hz), 122.8, 118.5 (q, *J* = 3.0 Hz). (Zinser, C. M.; Warren, K. G.; Meadows, R. E.; Nahra, F.; Al-Majid, A. M.; Barakat, A.; Islam, M. S.; Nolan, S. P.; Cazin, C. S. *J. Green Chem.* **2018**, *20*, 3246–3252.)

2-phenylpyridine (3ea)



General procedure was followed using sodium pyridine-2-sulfinate (165.0 mg, 1.0 mmol), PhMgBr (2.0 M in THF, 3.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 50/1) to afford product **3ea** as a colorless oil (82.0 mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ 8.69 (d, *J* = 4.8 Hz, 1H), 8.00–7.98 (m, 2H), 7.70 (dd, *J* = 3.6 Hz, 0.8 Hz, 2H), 7.49–7.44 (m, 2H), 7.42–7.38 (m, 1H), 7.20 (q, *J* = 4.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 157.4, 149.6, 139.4, 136.7, 128.9, 128.7, 126.9, 126.1, 120.5. (Rao, M. L. N.; Dhanorkar, R. J. *Eur. J. Org. Chem.* **2014**, 5214–5228.)

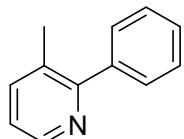
5-chloro-2-phenylpyridine (3fa)



General procedure was followed using sodium 5-chloropyridine-2-sulfinate (100.0 mg, 0.5 mmol), PhMgBr (2.0 M in THF, 1.5 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford

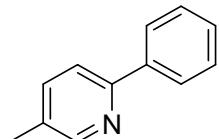
product **3fa** as a colorless oil (31.0 mg, 33%). ^1H NMR (400 MHz, CDCl_3) δ 8.64–8.64 (m, 1H), 7.97–7.95 (m, 2H), 7.74–7.66 (m, 2H), 7.50–7.43 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.6, 148.5, 138.2, 136.5, 130.6, 129.3, 128.9, 126.8, 121.1. (Rao, M. L. N.; Dhanorkar, R. *J. Eur. J. Org. Chem.* **2014**, 5214–5228.)

3-methyl-2-phenylpyridine (**3ga**)



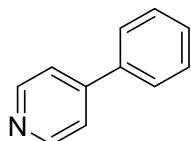
General procedure was followed using sodium 3-methylpyridine-2-sulfinate (179.0 mg, 1.0 mmol), PhMgBr (2.0 M in THF, 3.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ga** as a colorless oil (69.0 mg, 41%). ^1H NMR (400 MHz, CDCl_3) δ 8.51 (d, J = 4.4 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.17 (dd, J = 7.6 Hz, 4.8 Hz, 1H), 2.34 (s, 3H). (Rao, M. L. N.; Dhanorkar, R. *J. Eur. J. Org. Chem.* **2014**, 5214–5228.)

5-methyl-2-phenylpyridine (**3ha**)



General procedure was followed using sodium 5-methylpyridine-2-sulfinate (179.0 mg, 1.0 mmol), PhMgBr (2.0 M in THF, 3.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ha** as a white solid (41.0 mg, 24%). ^1H NMR (400 MHz, CDCl_3) δ 8.53 (s, 1H), 8.00–7.98 (m, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.52–7.44 (m, 3H), 7.41–7.37 (m, 1H), 2.34 (s, 3H). (Rao, M. L. N.; Dhanorkar, R. *J. Eur. J. Org. Chem.* **2014**, 5214–5228.)

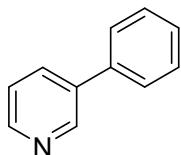
4-phenylpyridine (**3ia**)



General procedure was followed using sodium pyridine-4-sulfinate (165.0 mg, 1.0 mmol), PhMgBr (2.0 M in THF, 3.0 mmol). The crude product was purified by flash column

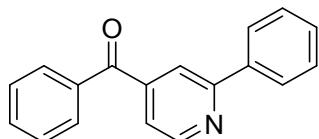
chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ia** as a yellow solid (70.0 mg, 45%). ¹H NMR (400 MHz, CDCl₃) δ 8.65 (dd, *J* = 4.4 Hz, 1.6 Hz, 2H), 7.64–7.61 (m, 2H), 7.50–7.41 (m, 5H). (Rao, M. L. N.; Dhanorkar, R. J. *Eur. J. Org. Chem.* **2014**, 5214–5228.)

3-phenylpyridine (3ja)



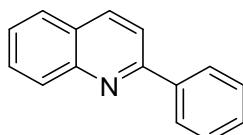
General procedure was followed using sodium pyridine-3-sulfinate (165.0 mg, 1.0 mmol), PhMgBr (2.0 M in THF, 3.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ja** as a colorless oil (54.0 mg, 35%). ¹H NMR (400 MHz, CDCl₃) δ 8.84 (d, *J* = 1.6 Hz, 1H), 8.58 (dd, *J* = 4.8 Hz, 1.6 Hz, 1H), 7.85 (dt, *J* = 8.0 Hz, 2.4 Hz, 1H), 7.56–7.53 (m, 2H), 7.47–7.43 (m, 2H), 7.40–7.35 (m, 1H), 7.34–7.30 (m, 1H). (Rao, M. L. N.; Dhanorkar, R. J. *Eur. J. Org. Chem.* **2014**, 5214–5228.)

phenyl(2-phenylpyridin-4-yl)methanone (3ka)



General procedure was followed using sodium 4-cyanopyridine-2-sulfinate (189.0 mg, 1.0 mmol) and PhMgBr (2.0 M in THF, 3.0 equiv). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10/1) to afford product **3ka** as a colorless oil (137.0 mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ 8.87 (d, *J* = 5.2 Hz, 1H), 8.05–8.02 (m, 3H), 7.88–7.86 (m, 2H), 7.68–7.64 (m, 1H), 7.55–7.45 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 195.4, 158.3, 150.1, 145.5, 138.6, 136.0, 133.6, 130.2, 129.6, 128.9, 128.7, 127.1, 121.3, 119.78. (Komeyama, K.; Nagao, Y.; Abe, M.; Takaki, K. *Chem. Soc. Jpn.* **2014**, 87, 301–313.)

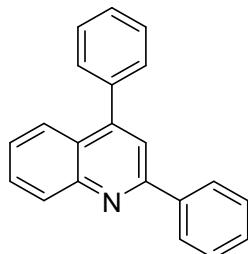
2-phenylquinoline (3la)



General procedure was followed using sodium quinoline-2-sulfinate (215.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3la** as a white solid (149.0 mg, 73%). ¹H NMR (400 MHz, CDCl₃) δ 8.23–8.17 (m, 4H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 6.8 Hz, 1H), 7.59–7.51 (m, 3H), 7.49–7.46 (m, 1H). ¹³C NMR (100 MHz,

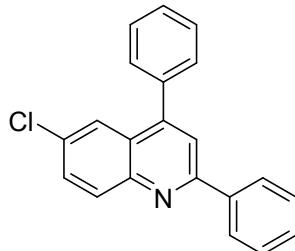
CDCl_3) δ 157.4, 148.3, 139.7, 136.8, 129.8, 129.7, 129.3, 128.9, 127.6, 127.5, 127.2, 126.3, 119.04. (Ji, X.; Huang, H.; Li, Y.; Chen, H.; Jiang, H. *Angew. Chem. Int. Ed.* **2012**, *51*, 7292-7296.)

2,4-diphenylquinoline (3ma)



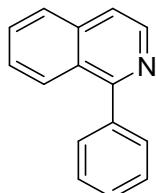
General procedure was followed using sodium 4-phenylquinoline-2-sulfinate (145.5 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ma** as a white solid (116.0 mg, 83%). ^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 7.6 Hz, 2H), 7.95 (d, J = 8.4 Hz, 1H), 7.85 (s, 1H), 7.77 (t, J = 7.2 Hz, 1H), 7.58–7.47 (m, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.9, 149.2, 148.9, 139.7, 138.5, 130.2, 129.6, 129.6, 129.4, 128.9, 128.6, 128.5, 127.6, 126.4, 125.8, 125.7, 119.4. (Ji, X.; Huang, H.; Li, Y.; Chen, H.; Jiang, H. *Angew. Chem. Int. Ed.* **2012**, *51*, 7292-7296.)

6-chloro-2,4-diphenylquinoline (3na)



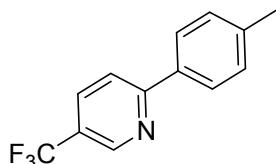
General procedure was followed using sodium 6-chloro-4-phenylquinoline-2-sulfinate (162.5 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3na** as a yellow solid (122.0 mg, 78%). mp 120-121 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.20–8.17 (m, 3H), 7.88 (t, J = 2.0 Hz, 1H), 7.85 (s, 1H), 7.68 (dd, J = 9.2, 2.4 Hz, 1H), 7.58–7.52 (m, 8H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.1, 148.5, 147.3, 139.2, 137.8, 132.2, 131.8, 130.5, 129.6, 129.5, 128.9, 128.8, 128.7, 127.6, 126.5, 124.5, 120.0. IR ν_{max} (KBr)/ cm^{-1} 3057, 1588, 1574, 1542, 1356, 1076, 885, 781, 754, 698. HRMS (ESI): m/z calcd. for $\text{C}_{21}\text{H}_{14}\text{ClN}$ $[\text{M}+\text{H}]^+$ 316.0888, found 316.0894.

1-phenylisoquinoline (3oa)



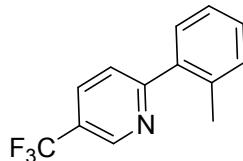
General procedure was followed using sodium isoquinoline-1-sulfinate (215.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3oa** as a white solid (170.0 mg, 83%). ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 5.2 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.70–7.62 (m, 4H), 7.52–7.50 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 160.7, 142.2, 139.6, 136.8, 129.9, 129.9, 128.6, 128.3, 127.5, 127.1, 127.0, 126.7, 119.9. (Yang, J.; Liu, S.; Zheng, J.-F.; Zhou, J. *Eur. J. Org. Chem.* **2012**, 6248–6259.)

2-(p-tolyl)-5-(trifluoromethyl)pyridine (**3ab**)



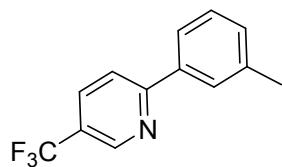
General procedure was followed using sodium 5-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ab** as a white solid (220.0 mg, 93%). ¹H NMR (400 MHz, CDCl₃) δ 8.92 (s, 1H), 7.95–7.93 (m, 3H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.3. ¹³C NMR (100 MHz, CDCl₃) δ 160.7, 146.6 (q, *J* = 4.0 Hz), 140.3, 135.2, 133.8 (q, *J* = 4.0 Hz), 129.7, 127.9 (q, *J* = 270.0 Hz), 127.2, 125.0 (q, *J* = 33.0 Hz), 119.6, 21.3. (Wang, Dan.; Chen, H.-G.; Tian, X.-C.; Liang, X.-X.; Chen, F.-Z.; Gao, Feng. *RSC Adv.* **2015**, 5, 107119–107122.)

2-(o-tolyl)-5-(trifluoromethyl)pyridine (**3ac**)



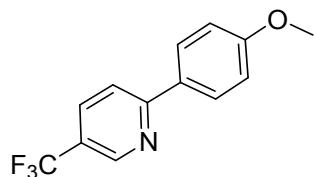
General procedure was followed using sodium 5-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ac** as a white solid (182.0 mg, 77%). ¹H NMR (400 MHz, CDCl₃) δ 8.97 (s, 1H), 8.00 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.36–7.28 (m, 3H), 2.38 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.3. ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 146.2 (q, *J* = 4.0 Hz), 139.1, 135.9, 133.4 (q, *J* = 3.0 Hz), 131.0, 130.6 (q, *J* = 272.7 Hz), 129.6, 129.1, 126.1, 125.0 (q, *J* = 33.0 Hz), 123.8, 20.3. (Wang, Dan.; Chen, H.-G.; Tian, X.-C.; Liang, X.-X.; Chen, F.-Z.; Gao, Feng. *RSC Adv.* **2015**, 5, 107119–107122.)

2-(m-tolyl)-5-(trifluoromethyl)pyridine (**3ad**)



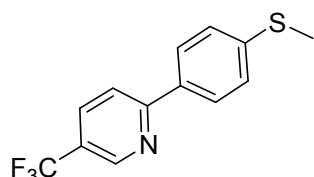
General procedure was followed using sodium 5-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ad** as a white solid (168.0 mg, 71%). ^1H NMR (400 MHz, CDCl_3) δ 8.94 (s, 1H), 7.96 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.87 (s, 1H), 7.83 (t, J = 8.8 Hz, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 2.46 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -62.3. ^{13}C NMR (100 MHz, CDCl_3) δ 160.9, 146.6 (q, J = 4.0 Hz), 138.7, 137.9, 133.9 (q, J = 3.0 Hz), 130.8, 128.9, 128.0, 121.8 (q, J = 270.0 Hz), 125.2 (q, J = 32.0 Hz), 124.4, 120.0, 21.5. (Wang, Dan.; Chen, H.-G.; Tian, X.-C.; Liang, X.-X.; Chen, F.-Z.; Gao, Feng. *RSC Adv.* **2015**, *5*, 107119-107122.)

2-(4-methoxyphenyl)-5-(trifluoromethyl)pyridine (3ae)



General procedure was followed using sodium 5-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ae** as a white solid (205.0 mg, 81%). ^1H NMR (400 MHz, CDCl_3) δ 8.87 (s, 1H), 7.99 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 3.85 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -62.2. ^{13}C NMR (100 MHz, CDCl_3) δ 161.4, 160.2, 146.5 (q, J = 3.0 Hz), 133.7 (q, J = 3.0 Hz), 130.5, 128.0, 127.9 (q, J = 270.0 Hz), 124.5 (q, J = 33.0 Hz), 119.0, 114.3, 55.4. (Wang, Dan.; Chen, H.-G.; Tian, X.-C.; Liang, X.-X.; Chen, F.-Z.; Gao, Feng. *RSC Adv.* **2015**, *5*, 107119-107122.)

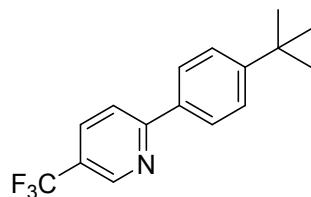
2-(4-(methylthio)phenyl)-5-(trifluoromethyl)pyridine (3af)



General procedure was followed using sodium 5-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3af** as a white solid (188.0 mg, 70%). ^1H NMR (400 MHz, CDCl_3) δ 8.89 (s, 1H), 7.95 (t, J = 8.4 Hz, 3H), 7.78 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 7.6 Hz, 2H), 2.51 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -62.3. ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 146.6 (q, J = 3.0 Hz), 141.6, 134.3, 133.9 (q, J = 4.0 Hz), 127.8 (q,

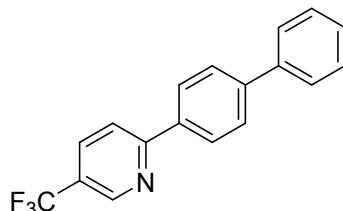
J = 270.0 Hz), 127.5, 126.2, 124.6 (q, *J* = 33.0 Hz), 119.4, 15.3. (Linke, S.; Manolikakès, S. M.; Auffrant, A.; Gosmini, C. *Synthesis* **2018**, *50*, 2595-2600.)

2-(4-(tert-butyl)phenyl)-5-(trifluoromethyl)pyridine (3ag)



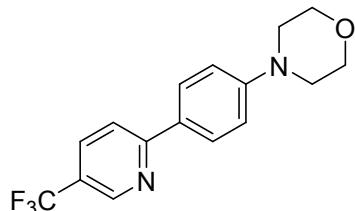
General procedure was followed using sodium 5-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ag** as a white solid (173.0 mg, 62%). ¹H NMR (400 MHz, CDCl₃) δ 8.92 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.94 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 1.36 (s, 9H). ¹⁹F NMR (375 MHz, CDCl₃) δ -69.6. ¹³C NMR (100 MHz, CDCl₃) δ 160.6, 153.5, 146.57 (q, *J* = 4.0 Hz), 135.2, 133.8 (q, *J* = 4.0 Hz), 127.9 (q, *J* = 270.0 Hz), 127.0, 125.9, 124.9 (q, *J* = 33.0 Hz), 119.6, 34.8, 31.2. (Wang, Dan.; Chen, H.-G.; Tian, X.-C.; Liang, X.-X.; Chen, F.-Z.; Gao, Feng. *RSC Adv.* **2015**, *5*, 107119-107122.)

2-([1,1'-biphenyl]-4-yl)-5-(trifluoromethyl)pyridine (3ah)



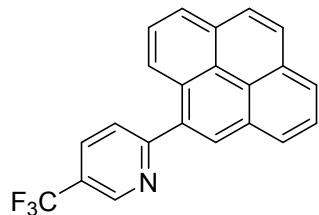
General procedure was followed using sodium 5-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ah** as a white solid (194.0 mg, 65%). ¹H NMR (400 MHz, CDCl₃) δ 8.97 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 2H), 8.00 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.70–7.64 (m, 2H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.2. ¹³C NMR (100 MHz, CDCl₃) δ 160.2, 146.7 (q, *J* = 3.0 Hz), 142.9, 140.3, 136.8, 133.9 (q, *J* = 4.0 Hz), 128.9, 127.9 (q, *J* = 270.0 Hz), 127.8, 127.7, 127.7, 127.1, 125.3 (q, *J* = 33.3 Hz), 119.81. (Deng, J. Z.; Paone, D. V.; Ginnetti, A. T.; Kurihara, H.; Dreher, S. D.; Weissman, S. A.; Stauffer, S. R.; Burgey, C. S. *Org. Lett.* **2009**, *11*, 345-347.)

4-(4-(trifluoromethyl)pyridin-2-yl)phenyl)morpholine (3ai)



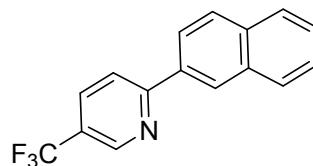
General procedure was followed using sodium 5-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 5/1) to afford product **3ai** as a white solid (209.0 mg, 68%). mp 218-220 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.87 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.90 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.89 (t, *J* = 4.8 Hz, 4H), 3.28 (t, *J* = 5.2 Hz, 4H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.1. ¹³C NMR (100 MHz, CDCl₃) δ 160.3, 152.5, 146.5 (q, *J* = 4.0 Hz), 133.7 (q, *J* = 4.0 Hz), 128.0 (q, *J* = 270.0 Hz), 128.8, 128.3, 123.7 (q, *J* = 33.0 Hz), 118.7, 115.0, 66.7, 48.4. IR ν_{max} (KBr)/cm⁻¹ 1596, 1123, 927, 824, 738. HRMS (ESI): m/z calcd. for C₁₆H₁₅F₃N₂O [M+H]⁺ 309.1209, found 309.1202.

2-(pyren-4-yl)-5-(trifluoromethyl)pyridine (**3aj**)



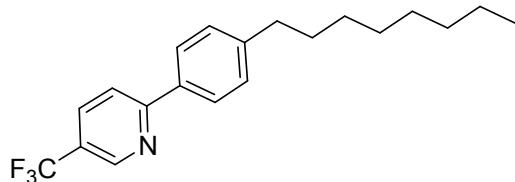
General procedure was followed using sodium 5-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3aj** as a white solid (176.0 mg, 51%). mp 117-118 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.16 (s, 1H), 8.35 (d, *J* = 9.2 Hz, 1H), 8.24 (d, *J* = 7.6 Hz, 1H), 8.21 (t, *J* = 8.4 Hz, 2H), 8.13-8.06 (m, 5H), 8.03 (t, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.1. ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 146.6 (q, *J* = 4.0 Hz), 134.0, 133.6 (q, *J* = 3.0 Hz), 132.0, 131.4, 130.8, 128.6, 128.6, 128.4, 127.9 (q, *J* = 270.0 Hz), 127.6, 127.3, 126.2, 125.7, 125.4, 125.3, 125.2 (q, *J* = 33.0 Hz), 125.1, 124.8, 124.7, 124.2. IR ν_{max} (KBr)/cm⁻¹ 3041, 1602, 1326, 1130, 842, 719. HRMS (ESI): m/z calcd. for C₂₂H₁₂F₃N [M+H]⁺ 348.0995, found 348.0990.

2-(naphthalen-2-yl)-5-(trifluoromethyl)pyridine (**3ak**)



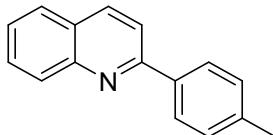
General procedure was followed using sodium 5-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10/1) to afford product **3ak** as a white solid (196.0 mg, 72%). mp 126-127 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.00 (s, 1H), 8.54 (s, 1H), 8.17 (d, *J* = 7.4 Hz, 1H), 8.03-7.96 (m, 4H), 7.91-7.88 (m, 1H), 7.56-7.54 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.2. ¹³C NMR (100 MHz, CDCl₃) δ 160.6, 146.7 (q, *J* = 4.0 Hz), 135.2, 134.1, 134.0 (q, *J* = 3.0 Hz), 133.4, 128.9, 128.8, 127.9 (q, *J* = 271.0 Hz), 127.7, 127.2, 127.2, 126.6, 125.3 (q, *J* = 33.0 Hz), 124.3, 120.2. IR ν_{max} (KBr)/cm⁻¹ 1604, 1275, 1115, 828, 765, 749. HRMS (ESI): m/z calcd. for C₁₆H₁₀F₃N [M+H]⁺ 274.0838, found 274.0835.

2-(4-octylphenyl)-5-(trifluoromethyl)pyridine (3al)



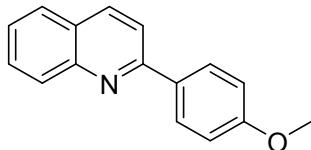
General procedure was followed using sodium 5-(trifluoromethyl)pyridine-2-sulfinate (233.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 50/1) to afford product **3al** as a yellow oil (241.0 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 8.93 (s, 1H), 7.97–7.94 (m, 3H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 1.70 (m, 2H), 1.33–1.28 (m, 10H), 0.91 (t, *J* = 6.8 Hz, 3H). ¹⁹F NMR (375 MHz, CDCl₃) δ -62.2. ¹³C NMR (100 MHz, CDCl₃) δ 160.7, 146.6 (q, *J* = 4.0 Hz), 145.4, 135.4, 133.8 (q, *J* = 3.0 Hz), 129.1, 127.9 (q, *J* = 270.0 Hz), 127.2, 125.0 (q, *J* = 33.0 Hz), 119.6, 35.9, 31.9, 31.3, 29.5, 29.3, 29.3, 22.7, 14.1. IR_ν_{max} (KBr)/cm⁻¹ 2926, 2855, 1579, 1166, 1131, 836, 767. HRMS (ESI): m/z calcd. for C₂₀H₂₄F₃N [M+H]⁺ 336.1934, found 336.1936.

2-(*p*-tolyl)quinoline (3lb)



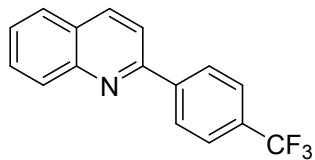
General procedure was followed using sodium quinoline-2-sulfinate (215.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3lb** as a white solid (164.0 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.16–8.11 (m, 3H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.76–7.72 (m, 1H), 7.54–7.50 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.3, 148.4, 139.4, 136.9, 136.7, 129.7, 129.6, 129.6, 127.5, 127.2, 126.1, 118.9, 21.4. (Bergmann, A. M.; Oldham, A. M.; Youa, W. Kevin Brown, M. *Chem. Commun.* **2018**, *54*, 5381–5384.)

2-(4-methoxyphenyl)quinoline (3le)



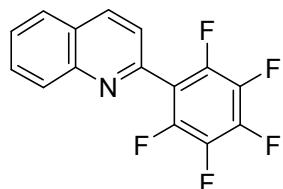
General procedure was followed using sodium quinoline-2-sulfinate (215.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3le** as a white solid (188.0 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ 8.18–8.14 (m, 4H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 9.2 Hz, 2H), 3.89 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 156.9, 148.3, 136.6, 132.3, 129.6, 128.9, 127.4, 126.9, 125.9, 118.5, 114.2, 55.4. (Ji, X.; Huang, H.; Li, Y.; Chen, H.; Jiang, H. *Angew. Chem. Int. Ed.* **2012**, *51*, 7292–7296.)

2-(4-(trifluoromethyl)phenyl)quinoline (3lm)



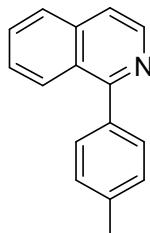
General procedure was followed using sodium quinoline-2-sulfinate (215.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3lm** as a white solid (180.0 mg, 66%).
 ^1H NMR (400 MHz, CDCl_3) δ 8.29 (d, J = 8.0 Hz, 2H), 8.25 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7.88 (t, J = 8.8 Hz, 2H), 7.79 (t, J = 8.4 Hz, 3H), 7.58 (t, J = 7.2 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -62.6. ^{13}C NMR (100 MHz, CDCl_3) δ 155.7, 148.3, 143.0, 137.1, 131.6 (q, J = 30.0 Hz), 130.0, 130.0, 128.3 (q, J = 270.0 Hz), 127.8, 127.5, 127.5, 126.9, 125.8 (q, J = 4.0 Hz), 118.78. (Ji, X.; Huang, H.; Li, Y.; Chen, H.; Jiang, H. *Angew. Chem. Int. Ed.* **2012**, *51*, 7292-7296.)

2-(perfluorophenyl)quinoline (3ln)



General procedure was followed using sodium isoquinoline-1-sulfinate (107.0 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ln** as a white solid (120.0 mg, 80%).
mp 87-88 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.68 (d, J = 5.6 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 5.6 Hz, 1H), 7.77-7.73 (m, 1H), 7.66-7.58 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -140.2 (m, 2F), -153.2 (t, J = 22.6 Hz, 1F), -161.4 (m, 2F). ^{13}C NMR (100 MHz, CDCl_3) δ 147.6, 146.1 (dm, J = 240.0 Hz), 142.9 (dm, J = 250.0 Hz), 142.6, 139.3 (dm, J = 250 Hz), 136.5, 130.8, 128.3, 127.9, 127.3, 125.6, 122.0, 114.1 (td, J = 10.0 Hz, 20.0 Hz). IR ν_{max} (KBr)/cm⁻¹ 3062, 1523, 1497, 988, 891, 827, 655. HRMS (ESI): m/z calcd. for $\text{C}_{15}\text{H}_6\text{F}_5\text{N}$ [M+H]⁺ 296.0493, found 296.0487.

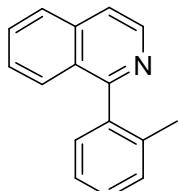
1-(p-tolyl)isoquinoline (3ob)



General procedure was followed using sodium isoquinoline-1-sulfinate (215.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3ob** as a yellow oil (209.0 mg, 95%).

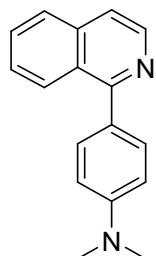
¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 5.6 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.69–7.66 (m, 1H), 7.63–7.60 (m, 3H), 7.54–7.50 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.6, 141.8, 138.6, 136.9, 136.3, 130.1, 129.8, 129.0, 127.7, 127.2, 126.9, 126.7, 119.8, 21.4. (Bergmann, A. M.; Oldham, A. M.; Youa, W. Kevin Brown, M. *Chem. Commun.* **2018**, *54*, 5381–5384.)

1-(o-tolyl)isoquinoline (3oc)



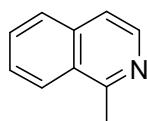
General procedure was followed using sodium isoquinoline-1-sulfinate (215.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3oc** was obtained as a yellow oil (130.0 mg, 73%). ¹H NMR (400 MHz, CDCl₃) δ 8.63 (d, *J* = 5.6 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.70–7.65 (m, 3H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.41–7.37 (m, 1H), 7.35–7.32 (m, 3H), 2.07 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.4, 142.1, 138.9, 136.4, 136.4, 130.2, 130.1, 129.5, 128.4, 127.5, 127.4, 127.2, 126.9, 125.6, 119.9, 19.8. (Bergmann, A. M.; Oldham, A. M.; Youa, W. Kevin Brown, M. *Chem. Commun.* **2018**, *54*, 5381–5384.)

4-(isoquinolin-1-yl)-N,N-dimethylaniline (3oo)



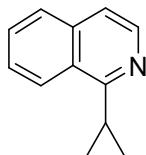
General procedure was followed using sodium isoquinoline-1-sulfinate (215.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 3/1) to afford product **3oo** as a white solid (203.0 mg, 82%). mp 111–112 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.58 (d, *J* = 5.6 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 3H), 7.56–7.50 (m, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 3.05 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 160.9, 150.8, 142.3, 137.1, 131.1, 129.7, 128.0, 127.6, 126.9, 126.7, 118.9, 112.0, 40.5. IR ν_{max} (KBr)/cm^{−1} 3044, 1609, 1525, 1352, 1193, 820, 753, 576. HRMS (ESI): m/z calcd. for C₁₇H₁₆N₂ [M+H]⁺ 249.1386, found 249.1399.

1-methylisoquinoline (3op)



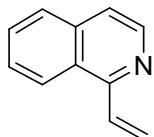
General procedure was followed using sodium isoquinoline-1-sulfinate (107.5 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3op** as a yellow oil (40.0 mg, 56%). ¹H NMR (400 MHz, CDCl₃) δ 8.37 (d, *J* = 3.2 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.65 (t, *J* = 6.4 Hz, 1H), 7.57 (t, *J* = 6.4 Hz, 1H), 7.47 (d, *J* = 4.0 Hz, 1H), 2.93 (s, 3H). (R.; Manna, S.; Zinken, S.; Kochnev, A. R.; Lukyanenko, E. R.; Kurkin, A. V.; Antonchick, A. P. *Chem. Commun.*, **2016**, 52, 12486-12489.)

1-cyclopropylisoquinoline (**3oq**)



General procedure was followed using sodium isoquinoline-1-sulfinate (215.0 mg, 1.0 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3oq** as a yellow oil (60.0 mg, 36%). ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 5.6 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.68 (td, *J* = 6.8 Hz, 1.2 Hz, 1H), 7.62–7.58 (m, 1H), 7.43 (d, *J* = 5.6 Hz, 1H), 2.77–2.70 (m, 1H), 1.29–1.25 (m, 2H), 1.14–1.10 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 161.8, 141.7, 135.9, 129.7, 127.7, 127.2, 126.9, 125.1, 118.4, 13.4, 9.4. (Thapa, S.; Kafle, A.; Gurung, S. K.; Montoya, A.; Riedel, P.; Giri, R. *Angew. Chem. Int. Ed.* **2015**, 54, 8236-8240.)

1-vinyliisoquinoline (**3or**)



General procedure was followed using sodium isoquinoline-1-sulfinate (107.5 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to afford product **3or** as a yellow oil (24.8 mg, 32%). ¹H NMR (400 MHz, CDCl₃) δ 8.53 (d, *J* = 5.6 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.68–7.56 (m, 4H), 6.55 (dd, *J* = 16.8, 2.0 Hz, 1H), 5.73 (dd, *J* = 10.4, 1.6 Hz, 1H). (Li, Y.; Guo, F.; Zha, Z.; Wang, Z. *Chem. Asian J.* **2013**, 8, 534-537.)

7. ICP-OES Analysis

1) ICP-OES Analysis

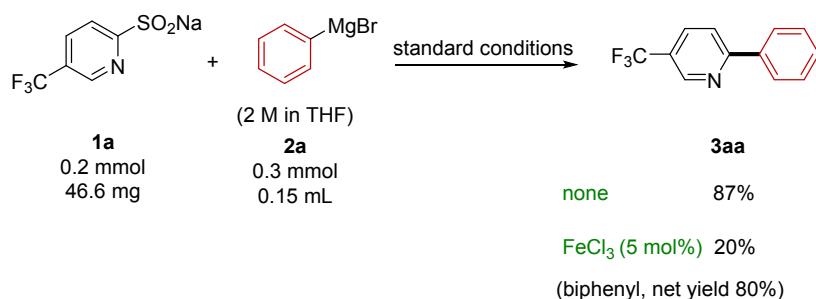
Under an atmosphere of N₂, PhMgBr (0.75 mmol) was added to a solution of sulfinate **1a** (0.5 mmol) in THF (2 mL), the resultant mixture was stirred for 10 min and solvent was removed in vacuo to give a solid. The crude solid (1.0 g) was dissolved with hydrochloric acid (2 mL)

and nitric acid (1 mL) and stirred at 350 °C. Then the resultant solution was diluted to 2 mL with pure water for ICP-OES determination.

Table S1. ICP-OES analysis of the reaction mixture

entry	Fe	Co	Ni	Cu	Pd
content (ppm)	26	<1	<1	<1	<1

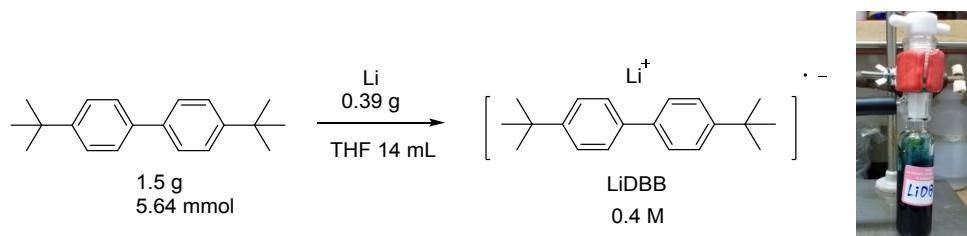
2) Effect of FeCl_3 (5 mol %)



Under an atmosphere of N_2 , sulfinate **1a** (0.2 mmol), FeCl_3 (5 mol %) and THF (1 mL) were successively added to a Schlenk tube. Then PhMgBr (0.3 mmol) was added, and the resultant mixture was stirred at room temperature for 12 h. Addition of H_2O (5 mL) was followed by extraction using EtOAc (5 mL). The yield of **3aa** was determined by ^{19}F NMR using PhOCF_3 as an internal standard. Then the combined organic layers were removed under reduced pressure and the residue was purified by column chromatography (100% petroleum ether) to furnish biphenyl (25 mg). In order to eliminate the influence of biphenyl contained in PhMgBr itself, we directly quenched the PhMgBr (0.15 mL) and only obtained 7 mg of biphenyl, indicating that the above biphenyl is derived from homocoupling of PhMgBr . We proposed that in the presence of FeCl_3 (5 mol%), oxidative homocoupling of PhMgBr preferentially proceeded, and biphenyl was formed as much as **3aa**. This fact shows that Fe drastically lowered the yield of **3aa**, so it is unlikely that the trace amount of Fe is involved in the coupling reaction between heteroaryl sulfinate with Grignard reagents.

8. Mechanistic Studies

(1) Preparation of LiDBB

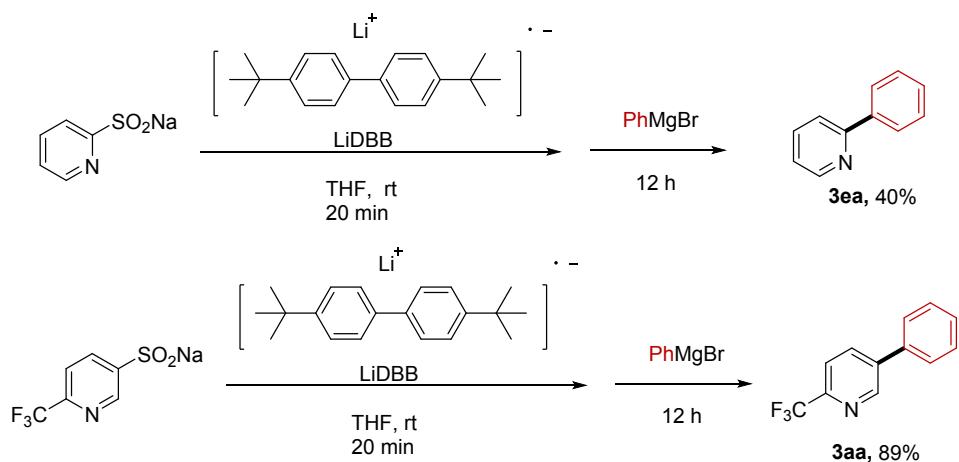


LiDBB was prepared by adding 4, 4'-ditert-butylbiphenyl (DBB, 1.50 g, 5.64 mmol, 1 equiv)

to a 50 mL sealed tube under an atmosphere of Ar. Then an ice bath was applied, and lithium wire (0.39 g, 56.4 mmol, 10 equiv) was clipped into the flask under a stream of argon. THF (14 mL) was added, and the solution turned green, darkening over for 5 h at 0 °C.

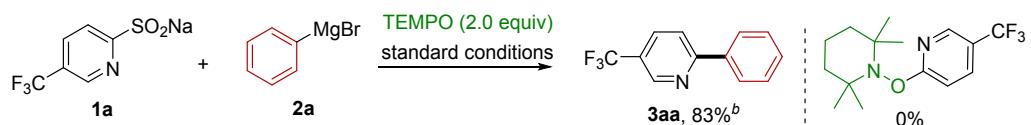
To a 50 mL volumetric flask, thioanisole (1.20 mL, 10.2 mmol) and THF were added to form a 0.20 M solution. A dry 10 mL flask was evacuated and backfilled with argon 3 times and cooled to 0 °C, and 1.00 mL of the 0.20 M thioanisole solution was added. LiDBB was then added dropwise until a persistent dark-green color was observed. The procedure was repeated three times, and the average volume added was used to calculate the molarity of the LiDBB. (Hill, R. R.; Rychnovsky, S. D. *J. Org. Chem.* **2016**, *81*, 10707–10714.)

(2) Effect of Single Electron Donors (LiDBB)



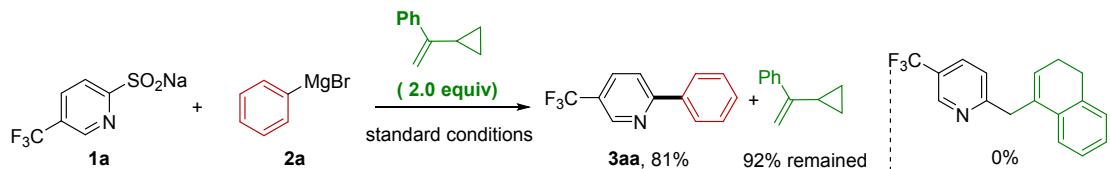
Under an atmosphere of Ar, sulfonates (0.5 mmol) and THF (2.0 mL) were successively added to a Schlenk tube. To the stirred solution was added LiDBB (0.25 mL, 0.40 M solution in THF, 0.1 mmol) at room temperature. After the mixture was stirred for 30 min, PhMgBr (1.5 mmol) was added. Then the resultant mixture was stirred at room temperature for 12 h. The yield was determined by ¹⁹F NMR using PhOCF₃ as an internal standard.

(3) Radical trapping experiments



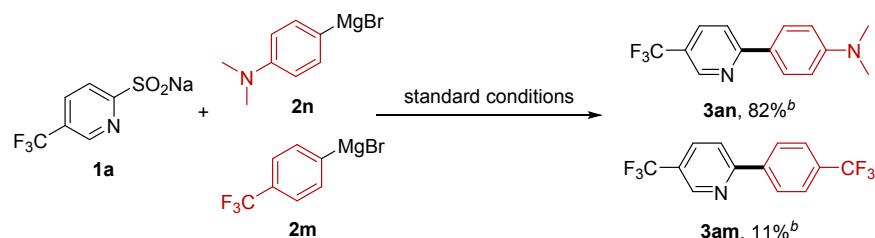
Under an atmosphere of N₂, sulfonate **1a** (0.5 mmol), TEMPO (1.0 mmol) and THF (2.0 mL) were successively added to a Schlenk tube. Then PhMgBr (1.5 mmol) was added, and the resultant mixture was stirred at room temperature for 12 h. The yield was determined by ¹⁹F NMR using PhOCF₃ as an internal standard.

(4) Radical clock reaction



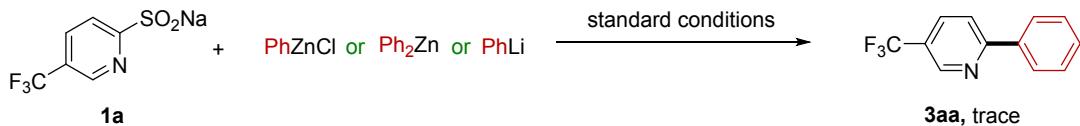
Under an atmosphere of N_2 , sulfinate **1a** (0.5 mmol), (1-cyclopropylvinyl)benzene (1.0 mmol) and THF (2.0 mL) were successively added to a Schlenk tube. Then PhMgBr (1.5 mmol) was added, and the resultant mixture was stirred at room temperature for 12 h. The yield of **3aa** was determined by ^{19}F NMR using PhOCF_3 as an internal standard, and 92% (1-cyclopropylvinyl)benzene was recovered by column chromatography.

(5) Competition experiments of $p\text{-Me}_2\text{NC}_6\text{H}_4\text{MgBr}$ and $p\text{-CF}_3\text{NC}_6\text{H}_4\text{MgBr}$



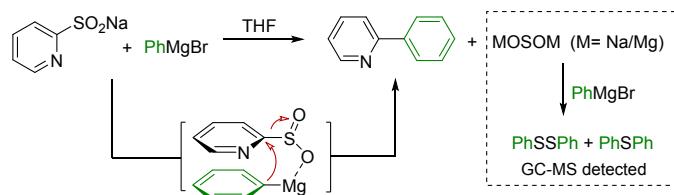
Under an atmosphere of N_2 , $p\text{-Me}_2\text{NC}_6\text{H}_4\text{MgBr}$ (1.5 equiv) and $p\text{-CF}_3\text{NC}_6\text{H}_4\text{MgBr}$ (1.5 equiv) were added to a solution of sulfinate (1.0 equiv) in THF. The mixture was stirred at room temperature for 12 hours. The yield was determined by ^{19}F NMR using PhOCF_3 as an internal standard.

(6) Reaction of sulfinate with Arylzinc reagents and PhLi



Under an atmosphere of N_2 , Arylzinc Reagent (1.5 equiv) or PhLi (1.5 equiv) was added to a solution of sulfinate (1.0 equiv) in THF. The mixture was stirred at room temperature for 12 hours. The yield was determined by ^{19}F NMR using PhOCF_3 as an internal standard.

(7) The proposed mechanism and the fate of leaving group

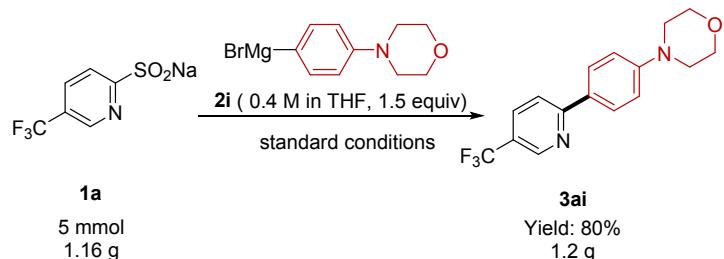


Scheme S1. The Proposed Mechanism

A plausible mechanism for the desulfinative cross-coupling of heteroaryl sulfinites with Grignard reagents is proposed in Scheme S1. First, The Mg^{2+} ion chelated with the oxygen atom

of sulfionates salts, which activates the C–S bond, then the simple addition on C-2 atom of pyridine ring, followed by elimination of sulphoxylate anion (SO_2^{2-}). (Hamilton, A. J.; Sutton, L. E. *Chem. Commun.* **1968**, *8*, 460.) To verify the proposed reaction mechanism shown in Scheme S1, we attempted to detect sulfur-containing fragments derived from leaving groups. In this reaction, two S-containing products PhSSPh and PhSPh were detected by the GC-MS when 1.2 equivalent of PhMgBr was applied. These observations imply that the sulphoxylate anion (SO_2^{2-}) would be reduced to thioether or disulfide under this conditions. Although there are sporadic reports on this aspect, the detailed fate of SO_2^{2-} is still not clear. Further research on the profiles of SO_2^{2-} is underway in our group. (a) Harpp, D. N.; Martin Vines, S.; Montillier, J. P.; Chan, T. H. *J. Org. Chem.* **1976**, *41*, 3987–3992. (b) Manya, P.; Sekera, A.; Rumpf, P. *Tetrahedron* **1970**, *26*, 467–476. (c) Davis, F. A.; Jenkins, L. A.; Billmers, R. L. *J. Org. Chem.* **1986**, *41*, 1033–1040.

11. Scale-up experiment



Under an atmosphere of N_2 , Grignard reagent **2i** (7.5 mmol, 0.4 M in THF, 1.5 equiv) was added to a solution of heteroaryl sulfinate **1a** (5.0 mmol, 1.0 equiv) in THF (20 mL). The mixture was stirred at room temperature for 12 hours. Addition of H_2O (10 mL) was followed by extraction using EtOAc (3×20 mL). Then the combined organic layers were removed under reduced pressure and the residue was purified by column chromatography (eluting with petroleum ether/ethyl acetate = 5/1) to furnish the target product.

12. Copies of NMR Spectra

