Supporting Information

Synthesis of Aryl Thiocyanates by Copper-catalyzed Aerobic Oxidative Cross-coupling of Arylboronic acids and KSCN

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General

All proton NMR and $^{13}$ C NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer in deuterium solvents with tetramethylsilane (TMS) as internal standard. High resolution mass spectra were recorded in the EI mode on Waters GCT Premier TOF mass spectrometer with an Agilent 6890 gas chromatography using a DB-XLB column (30 m x 0.25 mm (i.d.), 0.25 μ). IR spectra were recorded on a NICOLET AVATAR 370 FT-IR instrument. GC analyses were performed on a Thermo
TRACE GC Ultra instrument with FID detector using a HP-5 capillary column (30 m x 0.25 mm (i.d.), 0.25 μ). Flash column chromatography was performed on silica (200-300 mesh) with petroleum ether/ethyl acetate as eluent under protection of N₂. Melting points (uncorrected) were determined on BUCHI M-565 apparatus. All experiments were carried out in a closed Teflon-lined stainless steel autoclave (250 mL), the initial atmospheric air in the autoclave did not exchange for all reactions. Acetonitrile was treated with CaH₂ and fresh distilled before use. 3 Å MS was dried at 400-450 °C for 5 h before use. Other solvents and reagents were directly used without further purification.

**General procedure for the preparation of aryl thiocyanates (2a-2q)**

To a Teflon-lined stainless steel autoclave (250 mL), added aryl boronic acids (10 mmol), KSCN (11 mmol), Cu(OAc)₂ (2 mmol), 3 Å MS (2.5 g) and CH₃CN (25 mL). Then closed the autoclave and charged oxygen to 0.2 MPa. Put the autoclave into the oil bath, which was preheated to 80 °C. After the reaction proceeded in 12 hours, cooled down the autoclave to room temperature and carefully depressurized the autoclave. The mixture in the autoclave was filtrated to remove the catalyst and 3Å MS, and washed with CH₃CN. The combined filtrate was concentrated under reduced pressure. The residual was purified by flash chromatography through a silica column using petroleum ether/ethyl acetate as the eluent under the protection of N₂ to afford the desired aryl thiocyanates.

**Characterization data for aryl thiocyanates 2a-2o and 2q**

**Phenyl thiocyanates 2a.**

Yield: 90%. Yellowish oil; IR (neat): ν = 2173 cm⁻¹; ^1H NMR (500 MHz, CDCl₃): δ = 7.43-7.56 (m, 5H); ^13C NMR (125 MHz, CDCl₃): δ = 110.5, 124.4, 129.5, 130.06, 130.23; EI-HRMS m/z calcd for C₇H₅NS [M]⁺ 135.0143, found 135.0140. CAS Reg. No. 5285-87-0.
4-Phenylphenyl thiocyanate 2b
Yield: 91%. Yellow solid, mp: 81.1 °C (lit. [1] mp 84 °C); IR (KBr): ν = 2149 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 7.42-7.68 (m, 9H); ¹³C NMR (125 MHz, CDCl₃): δ = 110.5, 123.0, 127.1, 128.2, 128.88, 129.04, 130.6, 139.4, 142.9; EI-HRMS m/z calcd for C₁₃H₉NS [M]⁺ 211.0456, found 211.0458. CAS Reg. No. 99847-37-5.

2-Methoxyphenyl thiocyanate 2c
Yield: 70%. Yellow oil; IR (neat): ν = 2153 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 3.94 (s, 3H), 6.94-7.59 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ = 56.2, 110.5, 111.4, 113.1, 122.1, 129.9, 130.5, 156.5; EI-HRMS m/z calcd for C₈H₇NOS [M]⁺ 165.0248, found 165.0252. CAS Reg. No. 14372-66-8.

3-Methoxyphenyl thiocyanate 2d
Yield: 78%. Yellow oil; IR (neat): ν = 2149 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 3.85 (s, 3H), 6.94-7.36 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ = 55.6, 110.4, 115.1, 115.5, 122.0, 125.3, 131.0, 160.7; EI-HRMS m/z calcd for C₈H₇NOS [M]⁺ 165.0248, found 165.0242. CAS Reg. No. 14372-67-9.

4-Methoxyphenyl thiocyanate 2e
Yield: 80%. Yellow oil; IR (KBr): ν = 2149 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 3.84 (s, 3H), 6.95-7.53 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ = 55.5, 111.5, 113.9, 115.9, 133.8, 161.3; EI-HRMS m/z calcd for C₈H₇NOS [M]⁺ 165.0248, found 165.0251. CAS Reg. No. 5285-90-5.

2-Methylphenyl thiocyanate 2f
Yield: 74%. Yellow-wish oil; IR (neat): ν = 2149 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 2.50 (s, 3H),
7.28-7.65 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 20.3, 110.3, 123.6, 127.7, 130.2, 131.4, 131.9, 139.3; EI-HRMS $m/z$ calcd for C$_8$H$_7$NS [M]$^+$ 149.0299, found 149.0306. CAS Reg. No. 5285-88-1.

3-Methylphenyl thiocyanate 2g
Yield: 80%. Yellow oil; IR (neat): $\nu$ = 2153 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 2.40 (s, 3H), 7.22-7.36 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 21.3, 110.7, 124.0, 127.0, 129.96, 130.34, 130.46, 140.5; EI-HRMS $m/z$ calcd for C$_8$H$_7$NS [M]$^+$ 149.0299, found 149.0296. CAS Reg. No. 5285-89-2.

4-Methylphenyl thiocyanate 2h
Yield: 85%. Yellow oil; IR (neat): $\nu$ = 2153 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 2.39 (s, 3H), 7.25-7.45 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 21.2, 111.0, 120.5, 130.71, 130.97, 140.3; EI-HRMS $m/z$ calcd for C$_8$H$_7$NS [M]$^+$ 149.0299, found 149.0297. CAS Reg. No. 5285-89-2.

4-Fluorophenyl thiocyanate 2i
Yield: 78%. Colorless oil; IR (neat): $\nu$ = 2153 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.15-7.59 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 110.6, 117.6(d, $J$ = 22.7 Hz), 119.2(d, $J$ = 3.3 Hz), 133.2(d, $J$ = 8.9 Hz), 163.6(d, $J$ = 250.1 Hz); EI-HRMS $m/z$ calcd for C$_7$H$_4$NSF [M]$^+$ 153.0048, found 153.0048. CAS Reg. No. 2924-02-9.

4-Chlorophenyl thiocyanate 2j
Yield: 78%. White solid, mp: 34.2 °C (lit. [2] mp 36 °C); IR (KBr): $\nu$ = 2157 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.27-7.50 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 109.9, 122.7, 130.5, 131.5, 136.2; EI-HRMS $m/z$ calcd for C$_7$H$_4$NSCl [M]$^+$ 168.9753, found 168.9757. CAS Reg. No. 3226-37-7.
2-Bromophenyl thiocyanate 2k
Yield: 81%. Pink oil; IR (neat): $\tilde{\nu} = 2161$ cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.25-7.74$ (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 109.6$, 121.8, 127.1, 129.07, 129.44, 130.1, 133.6; EI-HRMS m/z calcd for C$_7$H$_4$NSBr [M]$^+$ 212.9248, found 212.9238. CAS Reg. No. 55757-32-9.

2,4-Dichlorophenyl thiocyanate 2l
Yield: 73%. Pink solid, mp: 68.4 °C (lit. [3] mp 72 °C); IR (KBr): $\tilde{\nu} = 2157$ cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.38-7.66$ (m, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 108.7$, 123.3, 128.8, 130.3, 130.8, 133.6, 136.1; EI-HRMS m/z calcd for C$_7$H$_3$NSCl$_2$ [M]$^+$ 202.9363, found 202.9366. CAS Reg. No. 3313-78-8.

4-Trifluorophenyl thiocyanate 2m
Yield: 80%. Colorless oil; IR (neat) $\tilde{\nu}$: 2157 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.64-7.73$ (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 108.9$, 123.4(q, $J = 271.3$ Hz), 127.1(q, $J = 3.8$ Hz), 129.1, 129.6, 131.5(q, $J = 32.5$ Hz); EI-HRMS m/z calcd for C$_8$H$_4$NF$_3$S [M]$^+$ 203.0017, found 203.0025. CAS Reg. No. 90348-21-3.

4-(Methoxycarbonyl)phenyl thiocyanate 2n
Yield: 59%. White soild, mp: 62.7 °C; IR (KBr): $\tilde{\nu} = 2153$, 1708 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 3.96$ (s, 3H), 7.57-8.12 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 52.6$, 109.1, 128.5, 130.47, 130.93, 131.21, 165.8; EI-HRMS m/z calcd for C$_9$H$_7$NO$_2$S [M]$^+$ 193.0198, found 193.0203. CAS Reg. No. 1879-22-7.

4-Acetylphenyl thiocyanate 2o
Yield: 25%. White solid, mp: 77.7 °C (lit. [4] mp 80.5-81.5 °C); IR (KBr): ν = 2153, 1675 cm⁻¹; "H NMR (500 MHz, CDCl₃): δ = 2.63 (s, 3H), 7.60-8.03 (m, 4H); "C NMR (125 MHz, CDCl₃): δ = 26.6, 109.0, 128.5, 129.8, 130.6, 137.3, 196.5; EI-HRMS m/z calcd for C₉H₇NOS [M]^+ 177.0248, found 177.0254. CAS Reg. No. 14428-56-9.

1-Naphthylthiocyanate 2q

Yield: 80%. Yellow solid, mp: 52.3 °C (lit. [2] mp 53 °C); IR (KBr): ν = 2149 cm⁻¹; "H NMR (500 MHz, CDCl₃): δ = 7.52-8.28 (m, 7H); "C NMR (125 MHz, CDCl₃): δ = 110.7, 120.8, 124.3, 125.9, 127.3, 128.1, 129.0, 131.6, 132.3, 132.4, 134.4; EI-HRMS m/z calcd for C₁₁H₇NS [M]^+ 185.0299, found 185.0307. CAS Reg. No. 16671-89-9.

References

Proton NMR and $^{13}$C NMR Spectra for aryl thiocyanates 2a-2o and 2q
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