Electronic Supplementary Information

Nickel Catalyzed Site Selective C–H Functionalization of α-Aryl-thioamides

Debashruti Bandyopadhyay, Annaram Thirupathi, Nagsen Munjaji Dhage, Nirmala Mohanta and S. Peruncheralathan*

School of Chemical Sciences, National Institute of Science Education and Research
Bhubaneswar, HBNI, Jatni, Khurda – 752050, India

Table of Contents: Page No.
General Consideration SI-2
General Procedure for the Synthesis of Thioanilides 3 SI-3
Ligand Screening of the Nickel Catalyzed Site Selective C—H Bond Functionalization of α-Aryl-thioacetanilide 3a SI-12
Oxidant Effect on Site Selective C—H Bond Functionalization of α-Aryl-thioacetanilide 3a SI-12
Procedure for the Site Selective C–H Functionalisation of α-Aryl-thioacetanilide 3 SI-13
General Procedure for the Synthesis of Thioamides 5 SI-22
General Procedure for Site Selective C–S Bond Formation of sp² C–H bond vs sp³ C–H bond SI-26
Controlled Experiments SI-30
A Plausible Mechanism for Nickel Catalyzed C—H Bond Functionalization SI-30
Crystal Data SI-31
References SI-32
NMR Spectra of the Isolated Products SI-33
High Resolution Mass Spectroscopy for Unknown Compounds SI-83

SI-1
Experimental Section:

General Considerations

Reagents

All reactions were performed by using standard vial technique with rubber septum. All solids were weighed in air. HFIP, Dioxane, KI, PIDA, were purchased from Aldrich, Spectrochem or Alfa-Aesar and used as received. NiBr$_2$ and Ad$_2$PBu were purchased from Aldrich. The isothiocyanates were purchased from Aldrich and noncommercial isothiocyanates were synthesized from the corresponding amines. All other reagents were purchased from common suppliers and used without further purification. Flash chromatography was performed using Merck Silica gel (230-400 mesh). Fractions were monitored by thin-layer chromatography on pre-coated silica gel $60F_{254}$ plates (Merck & co.) and were visualized by UV lamp.

Analytical Methods

NMR data were recorded on Bruker ARX 400 & 700 & 300 spectrometers. $^{13}$C and $^1$H NMR Spectrum were recorded in CDCl$_3$ and DMSO-$d_6$ referenced according to signals of deutero solvents. ESI HR-MS measurements were performed on Bruker micrOTOF-Q-II mass spectrometer. The X-ray quality crystals for the compounds 4a and 4b were grown by slow diffusion of n-hexane over CH$_2$Cl$_2$ solution. Single-crystal X-ray diffraction data of 4a and 4b were collected on a Rigaku SuperNova fine-focused dual diffractometer, with Cu Kα radiation ($\lambda = 1.54178$ Å) equipped with a PILATUS200K detector. Using Olex2, the structures 4a and 4b were solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms.
Scheme S1: General Procedure for the Synthesis of Thioanilides 3

To a stirring suspension of NaH (60% suspension in mineral oil) (1.2 equiv.) in DMF (10.0 mL) at 0 °C was added dropwise the corresponding benzyl nitrile (1 equiv.) in DMF (5.0 mL). After being further stirred for 1 h at room temperature, a solution of aryl isothiocyanate (1.1 equiv.) in DMF (5.0 mL) was added to the reaction mixture at 0 °C and followed by further stirring for 0.5 – 1 h at room temperature. After complete consumption of the starting materials (monitored by TLC), the reaction mixture was quenched with saturated NH₄Cl solution and extracted with EtOAc. The combined organic layer washed with water (3 x 25 mL) & brine (25 mL), dried over anhyd. Na₂SO₄ and concentrated under reduced pressure. The crude products were purified by flash chromatography using EtOAc/hexanes as eluent.

2-Cyano-2-(2,3-dimethoxyphenyl)-N-phenylethanethioamide (3a)

Reaction Time: 2 h

Yield: 87%

Melting Point: 137 – 139 °C.

Rf: 0.27 in 20% ethyl acetate in hexanes

IR (KBr): v (cm⁻¹) =3435, 3300, 3152, 3119, 2942, 2880, 2249, 1483, 1412, 1274, 1077, 996, 761, 742.

¹H NMR (300 MHz, CDCl₃) δ = δ 10.05 (s, 1H), 7.67 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.1 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.16 - 7.11 (m, 2H), 7.00 - 6.98 (m, 1H), 5.47 (s, 1H), 4.12 (s, 3H), 3.91 (s, 3H)

¹³C NMR (175 MHz, CDCl₃) δ = 191.4, 152.9, 145.4, 138.5, 129.0, 127.1, 126.2, 125.4, 123.0, 121.3, 117.4, 114.0, 61.6, 56.0, 51.0

HR-MS (ESI) Calcd for C₁₇H₁₆N₂O₂S [M+H]: 313.1005, found: 313.1007
2-Cyano-2-(3,4-dimethoxyphenyl)-N-phenylethanethioamide (3b)

![Chemical Structure]

- Reaction Time: 2 h
- Yield: 68%
- Melting Point: 134 - 136 °C.

Rf: 0.31 in 20% ethyl acetate in hexanes

IR (KBr): ν (cm⁻¹) = 3450, 3251, 2960, 2367, 2237, 1596, 1517, 1396, 1263, 1235, 1141, 1015, 746, 694.

¹H NMR (400 MHz, CDCl₃) δ = 9.19 (s, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.08 (s, 1H), 6.89 (d, J = 7.6 Hz, 1H), 5.34 (s, 1H), 3.87 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ = 191.7, 150.1, 149.8, 138.0, 129.0, 127.5, 123.9, 123.4, 120.7, 117.7, 111.7, 110.7, 56.2, 56.1, 54.3.

HR-MS (ESI) Calcd for C₁₇H₁₆N₂O₂S [M+Na]: 335.0825, found: 335.0816

2-Cyano-N-phenyl-2-(3,4,5-trimethoxyphenyl)ethanethioamide (3c)

- Reaction Time: 2 h
- Yield: 72%
- Melting Point: 144-146 °C.

Rf: 0.20 in 40% ethyl acetate in hexanes

IR (KBr): ν (cm⁻¹) = 3234, 2943, 2265, 1597, 1508, 1464, 1424, 1331, 1251, 1129.

¹H NMR (300 MHz, CDCl₃) δ = 8.77 (s, 1H), 7.35-7.20 (m, 2H), 7.14-7.01 (m, 2H), 7.00-6.91 (m, 1H), 6.48 (s, 2H), 5.02 (s, 1H), 3.55 (s, 9H).

¹³C NMR (75 MHz, CDCl₃) δ = 191.5, 153.7, 138.3, 138.0, 128.9, 127.6, 127.4, 123.4, 117.7, 105.0, 60.9, 56.2, 54.2.

HR-MS (ESI) Calcd for C₁₈H₁₈N₂O₃S [M+H]: 343.1111, Found: 343.1118
2-Cyano-2-(3,4-methylenedioxyphenyl)-N-phenylethanethioamide (3d)

Reaction Time: 2 h
Yield: 65%
Melting Point: 120 - 122 °C.

Rf: 0.34 in 25% ethyl acetate in hexanes

IR (KBr): ν (cm⁻¹) = 3434, 3176, 3082, 2965, 2361, 2197, 1598, 1503, 1487, 1443, 1250, 1101, 1038, 936, 854

¹H NMR (400 MHz, CDCl₃) δ = 9.04 (s, 1H), 7.58 (d, J = 7.6 Hz, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.29 - 7.25 (m, 1H), 7.10 - 7.01 (m, 2H), 6.90 - 6.83 (m, 1H), 6.02 (s, 2H), 5.29 (s, 1H).

¹³C NMR (100 MHz, CDCl₃) δ = 191.6, 149.0, 148.9, 137.9, 129.1, 127.6, 125.2, 123.6, 122.0, 117.5, 109.1, 108.1, 101.9, 54.3.

HR-MS (ESI) Calcd for C₁₆H₁₂N₂O₂S [M-H]: 295.0536, Found: 295.0584

2-Cyano-N-phenyl-2-(p-tolyl)ethanethioamide (3e)

Reaction Time: 2 h
Yield: 79%
Melting Point: 112 – 114 °C.

Rf: 0.35 in 20% ethyl acetate in hexanes

IR (KBr): ν (cm⁻¹) = 3181, 3123, 3012, 2972, 2192, 1598, 1541, 1512, 1493, 1409, 1268, 1108.

¹H NMR (300 MHz, DMSO) δ = 12.14 (s, 1H), 7.72 (d, J = 7.5 Hz, 2H), 7.54 (d, J = 7.5 Hz, 2H), 7.48 - 7.34 (m, 2H), 7.32 - 7.24 (m, 3H), 5.74 (s, 1H), 2.30 (s, 3H)

¹³C NMR (75 MHz, DMSO) δ = 192.8, 138.8, 138.2, 130.9, 129.5, 128.7, 127.3, 126.7, 123.2, 118.1, 51.9, 20.6.

HR-MS (ESI) Calcd for C₁₆H₁₄N₂S [M+Na]: 289.0770, found: 289.0803
2-(4-Chlorophenyl)-2-cyano-N-phenylethanethioamide (3f)

Reaction Time: 3 h

Yield: 56%

Melting Point: 124 – 126 °C.

Rf: 0.33 in 20% ethyl acetate in hexanes

IR (KBr): ν (cm⁻¹) = 3445, 3006, 2387, 2347, 2260, 1635, 1275, 1260, 764.

¹H NMR (400 MHz, CDCl₃) δ = 9.02 (s, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.36-7.25 (m, 4H), 7.18 (t, J = 7.2 Hz, 1H), 5.25 (s, 1H).

¹³C NMR (100 MHz, CDCl₃) δ = 190.8, 137.9, 136.0, 130.6, 130.0, 129.3 (2C), 127.9, 123.7, 117.0, 53.9.

HR-MS (ESI) Calcd for C₁₅H₁₁ClN₂S [M+H]: 287.0404, found: 287.0409

2-(4-Bromophenyl)-2-cyano-N-phenylethanethioamide (3g)

Reaction Time: 3 h

Yield: 67%, Yellowish orange solid

Melting point: 120 – 122 °C

Rf: 0.36 in 25% ethyl acetate in hexanes

IR (KBr): ν (cm⁻¹) = 3286, 3231, 2253, 195, 1519, 1412, 1398, 1105, 1073, 708.

¹H NMR (700 MHz, CDCl₃) δ = 8.96 (s, 1H), 7.61 (d, J = 7.7 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.0 Hz, 1H), 5.34 (s, 1H).

¹³C NMR (175 MHz, CDCl₃) δ = 190.72, 137.82, 132.94, 131.03, 129.52, 129.23, 127.86, 124.18, 123.73, 117.08, 53.94.


332.9879, found: 332.9853
2-Cyano-N-2-diphenylethanethioamide (3h)

Reaction Time: 2 h
Yield: 62%
Melting Point: 105 – 106 °C.

Rf: 0.36 in 25% ethyl acetate in hexanes

IR (KBr): ν (cm\(^{-1}\)) = 3450, 3274, 3141, 3095, 2252, 1598, 1558, 1492, 1403, 1279, 1118, 757

\(^1\)H NMR (400 MHZ, CDCl\(_3\)) \(\delta = 9.01\) (s, 1H), 7.61 – 7.55 (m, 4H), 7.48 - 7.46 (m, 3H), 7.37 (t, \(J = 7.7\) Hz, 2H), 7.29 - 7.25 (m, 1H), 5.39 (s, 1H).

\(^{13}\)C NMR (175 MHZ, CDCl\(_3\)) \(\delta = 191.3, 138.0, 131.9, 129.9, 129.8, 129.2, 128.0, 127.7, 123.7, 117.3, 54.8.

HR-MS (ESI) Calcd for C\(_{15}\)H\(_{12}\)N\(_2\)S [M+H]: 253.0794, found: 253.0809.

2-Cyano-2-(3,5-di-tert-butylphenyl)-N-phenylethanethioamide (3i)

Reaction Time: 2.5 h
Yield: 57%
Melting Point: 198 – 199 °C.

Rf: 0.30 in 30% ethyl acetate in hexanes

IR (KBr): 3261, 299, 2379, 2281, 1600, 1410, 1276, 1125

\(^1\)H NMR (300 MHz, DMSO) \(\delta = 12.13\) (s, 1H), 7.69 (d, \(J = 8.3\) Hz, 2H), 7.54 (s, 2H), 7.45-7.40 (m, 3H), 7.29 (d, \(J = 6.5\) Hz, 1H), 5.71 (s, 1H), 1.29 (s, 18H)

\(^{13}\)C NMR (175 MHZ, CDCl\(_3\)) \(\delta = 191.7, 152.9, 138.0, 130.7, 129.2, 127.6, 123.9, 123.5, 122.3, 117.6, 55.6, 35.2, 31.5.

HR-MS (ESI) Calcd for C\(_{23}\)H\(_{28}\)N\(_2\)S [M+Na]: 387.1865, Found: 387.1842

N-(2-chlorophenyl)-2-cyano-2-(3,4-dimethoxyphenyl)ethanethioamide (3j)

Reaction Time: 2 h
Yield: 65%
Melting Point: 141-142 °C.

Rf: 0.28 in 30% ethyl acetate in hexanes
IR (KBr): ν (cm⁻¹) = 3280, 2920, 2841, 2039, 1596, 1509, 1401, 1257, 1024.

¹H NMR (400 MHz, CDCl₃) δ = 9.06 (s, 1H), 8.46 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.04 (s, 1H), 6.95 (d, J = 8.4 Hz, 1H), 5.31 (s, 1H), 3.90 (s, 6H).

¹³C NMR (75 MHz, CDCl₃) δ = 191.8, 150.3, 149.9, 134.5, 129.6, 128.2, 127.2, 127.1, 124.9, 123.1, 121.0, 117.3, 111.7, 110.7, 56.1, 56.0, 54.8.

HR-MS (ESI) Calcd for C₁₇H₁₅ClN₂O₂S [M+H]: 347.0616, Found: 347.0603

2-Cyano-2-(3,4-dimethoxyphenyl)-N-(3,5-dimethylphenyl)ethanethioamide (3k)

Reaction Time: 3 h
Yield: 55%
Melting Point: 167-169 ºC

Rf: 0.30 in 20% ethyl acetate in hexanes

IR (KBr): ν (cm⁻¹) = 3666, 3250, 2910, 2250, 2064, 1565, 1480, 1260, 1090.

¹H NMR (700 MHz, DMSO) δ = 11.92 (s, 1H), 7.29 (s, 2H), 7.24 (s, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.90 (s, 1H), 5.64 (s, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 2.25 (s, 6H)

¹³C NMR (175 MHz, DMSO) δ = 192.8, 149.2, 148.7, 138.8, 138.0, 126.0, 120.9, 120.0, 118.3, 112.0, 111.3, 55.6, 55.6, 51.9, 20.9.

HR-MS (ESI) Calcd for C₁₉H₂₀N₂O₂S [M+H]: 341.1318, Found: 341.1317

2-Cyano-N-(2-(trifluoromethyl)phenyl)-2-(3,4,5-trimethoxyphenyl)ethanethioamide (3l)

Reaction Time: 2 h
Yield: 58%
Melting Point: 117-119 ºC.

Rf: 0.23 in 30% ethyl acetate in hexanes

IR (KBr): ν (cm⁻¹) = 3752, 3322, 3272, 2973, 2941, 2843, 2260, 1596, 1506, 1462, 1320, 1126, 1060, 1006.

¹H NMR (400 MHz, CDCl₃) δ = 8.78 (s, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 6.76 (s, 2H), 5.32 (s, 1H), 3.88 (s, 6H), 3.86 (s, 3H).
$^{13}$C NMR (175 MHz, CDCl$_3$) δ = 193.6, 154.4, 139.3, 135.5, 132.7, 128.9, 128.2, 126.7 (q, $J = 5.3$ Hz), 125.9, 124.6 (q, $J = 29.8$ Hz), 123.2 (q, $J = 271.9$ Hz), 116.9, 105.3, 61.0, 56.4, 54.8.

HR-MS (ESI) Calcd for C$_{19}$H$_{17}$F$_3$N$_2$O$_3$S [M+H]: 411.0985, Found: 411.0968

2-Cyano-N-(4-fluorophenyl)-2-(3,4,5-trimethoxyphenyl)ethanethioamide (3m)

IR (KBr): ν (cm$^{-1}$) = 3536, 3272, 2940, 2838, 2249, 1595, 1422, 1127, 837.

$^1$H NMR (300 MHz, CDCl$_3$) δ = 9.11 (s, 1H), 7.53 (s, 2H), 7.06 (t, $J = 7.8$ Hz, 2H), 6.79 (s, 2H), 5.36 (s, 1H), 3.87 (s, 9H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ = 191.9, 161.1 (d, $J = 246.1$ Hz), 153.9, 138.7, 134.1 (d, $J = 2.6$ Hz), 127.3, 125.8 (d, $J = 8.2$ Hz), 117.5, 115.9 (d, $J = 22.8$ Hz), 105.1, 61.0, 56.4, 54.2.

HR-MS (ESI) Calcd for C$_{18}$H$_{17}$N$_2$O$_3$F [M+H]: 361.1017, Found: 361.0999

2-Cyano-N-(3,5-dimethylphenyl)-2-(3,4-methylenedioxyphenyl)ethanethioamide (3n)

IR (KBr): ν (cm$^{-1}$) = 3327, 3236, 2247, 1504, 1415, 1293, 1254, 1098, 1040.

$^1$H NMR (300 MHz, CDCl$_3$) δ = 8.88 (s, 1H), 7.17 (s, 2H), 7.09 – 6.97 (m, 2H), 6.95 – 6.80 (m, 2H), 6.02 (s, 2H), 5.23 (s, 1H), 2.30 (s, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ = 191.3, 148.9, 148.8, 138.9, 137.8, 129.4, 125.3, 121.9, 121.2, 117.6, 109.1, 108.1, 101.9, 54.2, 21.3.

HR-MS (ESI) Calcd for C$_{18}$H$_{17}$N$_2$O$_3$S [M+H]: 325.1005, Found: 325.1002
2-Cyano-2-(3,4-methylenedioxyphenyl)-N-(m-tolyl)ethanethioamide (3o)

![Chemical Structure](image)

**Reaction Time:** 2 h  
**Yield:** 63%  
**Melting Point:** 137-139 °C.

**Rf:** 0.19 in 30% in ethyl acetate in hexanes

**IR (KBr):** \( \nu (\text{cm}^{-1}) = 3123, 2943, 2231, 1842, 1486, 1246, 1217, 1040. \)

**\(^1\)H NMR (400 MHz, CDCl\(_3\))**  
\( \delta = 9.10 (s, 1H), 7.43 (d, J = 8.0 \text{ Hz}, 1H), 7.39 (s, 1H), 7.29 (t, J = 4.4 \text{ Hz}, 1H), 7.14-7.05 (m, 3H), 6.88 (d, J = 8.4 \text{ Hz}, 1H), 6.04 (s, 2H), 5.30 (s, 1H), 2.36 (s, 3H). \)

**\(^{13}\)C NMR (175 MHz, CDCl\(_3\))**  
\( \delta = 191.5, 148.9, 148.8, 139.2, 137.9, 128.9, 128.4, 125.4, 124.01, 121.9, 120.7, 117.6, 109.1, 108.1, 101.9, 54.1, 21.4. \)

**HR-MS (ESI)** Calcd for C\(_{17}\)H\(_{14}\)N\(_2\)O\(_2\)S [M+H]: 311.0849, Found: 311.0832

2-Cyano-N-(4-isopropylphenyl)-2-phenylethanethioamide (3p)

![Chemical Structure](image)

**Reaction Time:** 3 h  
**Yield:** 40%  
**Melting Point:** 104 – 106 °C.

**Rf:** 0.35 in 20% ethyl acetate in hexanes

**IR (KBr):**  
\( \nu (\text{cm}^{-1}) = 3447, 2961, 2898, 2344, 2268, 1635, 1558, 1506, 1269, 784. \)

**\(^1\)H NMR (700 MHz, DMSO)\**  
\( \delta = 12.10 (s, 1H), 7.67 – 7.61 (m, 4H), 7.45 (t, J = 7.7 \text{ Hz}, 2H), 7.41 (t, J = 7.7 \text{ Hz}, 1H), 7.28 (d, J = 8.4 \text{ Hz}, 2H), 5.77 (s, 1H), 2.92 – 2.85 (m, 1H), 1.19 (d, J = 7.0 \text{ Hz}, 6H) \)

**\(^{13}\)C NMR (175 MHz, CDCl\(_3\))**  
\( \delta = 191.0, 148.5, 135.8, 132.1, 129.8, 129.7, 128.0, 127.0, 123.5, 117.4, 54.6, 33.9, 23.9. \)

**HR-MS (ESI)** Calcd for C\(_{18}\)H\(_{18}\)N\(_2\)S [M+H]: 295.1263, Found: 295.1280
2-Cyano-N-(3-methoxyphenyl)-2-phenylethioamide (3q)

Reaction Time: 3 h
Yield: 60%
Rf: 0.25 in 20% ethyl acetate in hexanes

^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta = 9.57 \) (s, 1H), 7.66 – 7.58 (m, 2H), 7.47 – 7.37 (m, 4H), 7.24 (t, \( J = 8.0 \) Hz, 1H), 7.10 (d, \( J = 8.0 \) Hz, 1H), 6.84 – 6.76 (m, 1H), 5.43 (s, 1H), 3.74 (s, 3H).

^1^3^C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta = 191.5, 159.7, 139.1, 132.1, 129.7, 129.5, 127.8, 117.8, 115.5, 113.1, 109.0, 55.4, 54.2.\)

HR-MS (ESI) Calcd. for C\textsubscript{16}H\textsubscript{14}N\textsubscript{2}OS [M+H]: 283.0900, Found: 283.1093

2-Cyano-N-(3-methoxyphenyl)-2-(3-trifluoromethylphenyl)ethanethioamide (3r)

Reaction Time: 3 h
Yield: 55%

Rf: 0.32 in 30% ethyl acetate in hexanes

^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta = 9.39 \) (s, 1H), 7.90 – 7.79 (m, 2H), 7.69 (d, \( J = 7.6 \) Hz, 1H), 7.58 (t, \( J = 7.6 \) Hz, 1H), 7.39 (s, 1H), 7.31 – 7.22 (m, 1H), 7.09 (d, \( J = 7.6 \) Hz, 1H), 6.82 (d, \( J = 8.0 \) Hz, 1H), 5.48 (s, 1H), 3.77 (s, 3H)

^1^3^C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta = 189.9, 160.0, 138.9, 133.3, 131.9 \) (q, \( J = 32.0 \) Hz), 131.2, 130.1, 129.8, 126.4 (q, \( J = 4.0 \) Hz), 124.6 (q, \( J = 4.0 \) Hz), 123.6 (q, \( J = 271 \) Hz), 116.7, 115.5, 113.4, 109.1, 55.4, 53.8.

HR-MS (ESI) Calcd for C\textsubscript{17}H\textsubscript{13}F\textsubscript{3}N\textsubscript{2}OS [M+H]: 351.0773, Found: 351.0932
Table S1. Ligand Screening of the Nickel Catalyzed Site Selective C—H Bond Functionalization of α-Aryl-thioacetanilide 3\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Yield of 4a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PPh\textsubscript{3} (4 mol%)</td>
<td>35%</td>
</tr>
<tr>
<td>2.</td>
<td>P(2-furyl)\textsubscript{3} (4 mol%)</td>
<td>37%</td>
</tr>
<tr>
<td>3.</td>
<td>Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2} (4 mol%)</td>
<td>40%</td>
</tr>
<tr>
<td>4.</td>
<td>HP(Cy)\textsubscript{3}BF\textsubscript{4} (4 mol%)</td>
<td>38%</td>
</tr>
<tr>
<td>5.</td>
<td>P(2-tolyl)\textsubscript{3} (4 mol%)</td>
<td>30%</td>
</tr>
<tr>
<td>6.</td>
<td>Ad\textsubscript{2}PBu (4 mol%)</td>
<td>52%</td>
</tr>
<tr>
<td>7.</td>
<td>Ad\textsubscript{2}PBu (4 mol%)</td>
<td>52%\textsuperscript{c}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: 3a (0.5 mmol), NiBr\textsubscript{2} (2 mol%), KI (2 equiv), PIDA (1 equiv), Ligand (4 mol%), HFIP (2.0 mL), temperature, 1-2 h. \textsuperscript{b}Isolated yields. \textsuperscript{c}PIDA (1.5 equiv) was used. HFIP-Hexafluoroisopropanol

Table S2. Oxidant Effect on Site Selective C—H Bond Functionalization of α-Aryl-thioacetanilide 3a\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant</th>
<th>Yield of 4a</th>
<th>Yield of 3a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PIDA (50 mol%)</td>
<td>24%</td>
<td>37%</td>
</tr>
<tr>
<td>2.</td>
<td>PIDA (20 mol%)</td>
<td>11%</td>
<td>56%</td>
</tr>
<tr>
<td>3.</td>
<td>TBHP (100 mol%)</td>
<td>30%</td>
<td>20%</td>
</tr>
<tr>
<td>4.</td>
<td>PIFA (100 mol%)</td>
<td>43%</td>
<td>35%\textsuperscript{c}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: 3a (0.5 mmol), NiBr\textsubscript{2} (2 mol%), KI (2 equiv), Oxidant (X mol%), HFIP (2.0 mL), temperature, 1-2 h. \textsuperscript{b}Isolated yields. HFIP- Hexafluoroisopropanol
General Procedure for Nickel Catalyzed Site Selective C—H Functionalization of α-Aryl-thioacetonilide 3 for the Synthesis of 2-Aminobenzob|b|thiophenes 4

An oven-dried 8 mL reaction vial was charged with NiBr₂ (2 mol%), PIDA (0.5 mmol) and KI (1 mmol), respective thioamide (0.5 mmol) in HFIP (2.0 mL) and was stirred at 50 °C for 1-3 h. The reaction mixture was monitored by TLC. After the starting material had been completely consumed, the reaction mixture was purified by flash chromatography.

3-Cyano-4,5-dimethoxy-2-(phenylamino)benzo[|b|]thiophene (4a)

Reaction Time: 1 h

Yield: 62%

Melting Point: 196-198 °C.

R₁ = 0.34 in 20% ethyl acetate in hexanes

IR (KBr): 3436, 3243, 3138, 3088, 2209, 1597, 1556, 1464, 1440, 1417, 1265, 1039

1H NMR (700 MHz, DMSO) δ = 10.05 (s, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.40 - 7.39 (m, 4H), 7.17 – 7.14 (m, 1H), 7.03 (d, J = 8.4 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H).

13C NMR (175 MHz, CDCl₃) δ = 161.81, 150.91, 141.71, 139.97, 131.47, 129.88, 125.20, 122.25, 120.27, 117.57, 116.23, 110.57, 81.24, 61.82, 56.79.

HR-MS (ESI) Calcd for C₁₇H₁₄N₂O₂S [M+H]: 311.0849, found: 311.0871

3-Cyano-5,6-dimethoxy-2-(phenylamino)benzo[|b|]thiophene (4b)

Reaction Time: 2 h

Yield: 59%

Melting Point: 180 – 182 °C.

R₁: 0.32 in 25% ethyl acetate in hexane
IR (KBr): 3272, 2993, 2963, 2199, 1601, 1562, 1491, 1474, 1461, 1435, 1402, 1298, 1246, 1208, 1173, 1083, 960, 836, 762, 700, 621

$^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 7.41 – 7.37 (m, 2H), 7.31 – 7.29 (m, 2H), 7.18 – 7.14 (m, 1H), 7.09 (s, 1H), 7.06 (s, 1H), 7.04 (s, 1H), 3.96 (s, 3H), 3.90 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 158.6, 149.5, 147.6, 140.4, 129.9, 129.8, 124.6, 121.1, 119.4, 115.5, 104.6, 102.4, 85.1, 56.5, 56.3

HR-MS (ESI) Calcd for C$_{17}$H$_{14}$N$_2$O$_2$S [M+H]: 311.0849, Found: 311.0890

3-Cyano-2-(phenylamino)-5,6,7-trimethoxybenzo[b]thiophene (4c)

**Reaction Time:** 1.5 h  
**Yield:** 67%  
**Melting Point:** 167-170°C  
$R_f =$ 0.33 in 20% ethyl acetate in hexanes  

IR (KBr): 3441, 3056, 2984, 2307, 2240, 1635, 1558, 1507, 1110, 895.

$^1$H NMR (700 MHz, CDCl$_3$) $\delta =$ 7.48 (s, 1H), 7.40 (t, $J =$ 7.7 Hz, 2H), 7.35 (d, $J =$ 7.7 Hz, 2H), 7.17 (t, $J =$ 7.7 Hz, 1H), 6.83 (s, 1H), 4.02 (s, 3H), 3.92 (s, 3H), 3.87 (s, 3H).

$^{13}$C NMR (175 MHz, CDCl$_3$) $\delta =$ 160.7, 154.2, 147.3, 140.2, 138.2, 132.4, 129.8, 124.9, 120.0, 115.6, 114.1, 97.8, 84.3, 61.5, 61.0, 56.4.

HR-MS (ESI) Calcd for C$_{18}$H$_{16}$N$_2$O$_3$S [M+Na]: 363.0774, Found: 363.0799

3-Cyano-5,6-methylenedioxy-2-(phenylamino)benzo[b]thiophene (4d)

**Reaction Time:** 1 h  
**Yield:** 61%  
**Melting Point:** 222 – 225 °C  
$R_f =$ 0.37 in 20% ethyl acetate in hexane  

IR (KBr): 3441, 3255, 2371, 2345, 2204, 1561, 1474, 1295, 1052, 945, 823, 695

SI-14
$^1$H NMR (400 MHz, DMSO) $\delta = 9.97$ (s, 1H), 7.41 (s, 1H), 7.39 – 7.34 (m, 4H), 7.10 (t, $J = 5.9$ Hz, 1H), 6.99 (s, 1H), 6.07 (s, 2H).

$^{13}$C NMR (100 MHz, DMSO) $\delta = 158.9, 147.3, 145.2, 141.4, 130.7, 129.4, 123.6, 121.2, 119.4, 114.9, 102.7, 101.4, 98.9, 84.3$.

HR-MS (ESI) Calcd for C$_{16}$H$_{10}$N$_2$O$_2$S [M+Na]: 317.0355, Found: 317.0362

3-Cyano-6-methyl-2-(phenylamino)benzo[b]thiophene (4e)

Reaction Time: 1 h
Yield: 60%
Melting Point: 155-157 °C.
$R_f = 0.25$ in 10% ethyl acetate in hexanes

IR (KBr): 3248, 2368, 2213, 1597, 1567, 1475, 1323, 757, 696

$^1$H NMR (700 MHz, CDCl$_3$) $\delta = 7.45$ (d, $J = 8.4$ Hz, 1H), 7.43 (brs, 1H), 7.42-7.39 (m, 2H), 7.37-7.33 (m, 3H), 7.21 - 7.17 (m, 2H), 2.42 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 159.8, 140.3, 134.0, 133.7, 129.8, 129.4, 127.5, 124.8, 121.9, 119.9, 119.5, 115.6, 83.7, 21.5$.

HR-MS (ESI) Calcd for C$_{16}$H$_{12}$N$_2$S [M+H]: 265.0794, Found: 265.0790

6-Chloro-3-cyano-2-(phenylamino)benzo[b]thiophene (4f)

Reaction Time: 1 h
Yield: 25%
Melting Point: 182 – 184 °C.
$R_f = 0.30$ in 10% ethyl acetate in hexanes

IR (KBr): 3678, 3253, 2920, 2211, 1604, 1567, 1464, 1397, 1247, 1062, 750, 694

$^1$H NMR (700 MHz, DMSO) $\delta = 10.35$ (s, 1H), 7.96 (s, 1H), 7.55 – 7.31 (m, 6H), 7.19 (t, $J = 7.0$ Hz, 1H)

SI-15
13C NMR (100 MHz, DMSO) δ = 161.5, 140.7, 135.9, 129.8, 129.5, 127.5, 126.4, 124.8, 122.2, 120.8, 119.8, 114.7, 81.5.

HR-MS (ESI) Calcd for C15H9ClN2S [M+H]: 285.0248, Found: 285.0238

3-Cyano-6-bromo-2-(phenylamino)benzo[b]thiophene (4g)

Reaction Time: 2 h
Yield: 20%
Melting Point: 200 – 202 °C

Rf: 0.33 in 15% ethyl acetate in hexanes

IR (KBr): ν (cm⁻¹): 3211, 2328, 2209, 1601, 1556, 1461, 1391, 1249, 1058.

1H NMR (400 MHz, CDCl₃) δ = 7.71 (s, 1H), 7.56 – 7.48 (m, 2H), 7.47 - 7.43 (m, 2H), 7.36 (d, J = 7.6 Hz, 2H), 7.30 - 7.23 (m, 2H).

13C NMR (175 MHz, DMSO-D₆) δ = 161.4, 140.6, 136.2, 130.1, 129.5, 129.0, 124.9, 124.8, 120.8, 120.1, 115.2, 114.6, 81.5.

HR-MS (ESI): Calcd. for C₁₅H₉BrN₂S (M+H): 328.9743 and 330.9722

Found: 328.9759 and 330.9743

3-Cyano-2-(Phenylamino)benzo[b]thiophene (4h)²

Reaction Time: 3 h
Yield: 41%
Melting Point: 134-136 °C.

Rf = 0.23 in 10% ethyl acetate in hexanes

IR (KBr): 3376, 2291, 1570, 1136

1H NMR (400 MHz, CDCl₃) δ = 7.61 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.51 (s, 1H), 7.44 – 7.36 (m, 5H), 7.25 – 7.19 (m, 2H).

13C NMR (100 MHz, CDCl₃) δ = 160.7, 140.1, 136.6, 129.9, 129.1, 126.2, 125.2, 123.8, 122.0, 120.3, 119.8, 115.4, 83.8.

HR-MS (ESI) Calcd for C₁₅H₁₀N₂S [M+H]: 265.0794, Found: 265.0780
3-Cyano-5,7-di-tert-butyl-2-(phenylamino)benzo[b]thiophene (4i)

![Chemical structure of 3-Cyano-5,7-di-tert-butyl-2-(phenylamino)benzo[b]thiophene (4i)]

**Reaction Time:** 1h  
**Yield:** 55%  
**Melting Point:** 235-237 °C.  
**R<sub>f</sub>** = 0.28 in 10% ethyl acetate in hexanes  

IR (KBr): 3122, 2961, 2321, 2231, 1596, 1561, 1415, 1309, 1252, 863  

<sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ = 7.39 (s, 1H), 7.32 (t, J = 7.7 Hz, 2H), 7.27 (d, J = 7.7 Hz, 2H), 7.19 (s, 1H), 7.15 (brs, 1H), 7.08 (t, J = 7.7 Hz, 1H), 1.38 (s, 9H), 1.29 (s, 9H).  

<sup>13</sup>C NMR (175 MHz, CDCl<sub>3</sub>) δ = 159.3, 149.7, 144.3, 140.3, 137.6, 129.9, 124.7, 123.5, 119.8, 119.3, 115.9, 114.9, 84.8, 35.9, 35.1, 31.7, 29.8.  

HR-MS (ESI) Calcd. for C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>S [M+Na]: 385.1709, Found: 385.1712  

2-[(2-Chlorophenyl)amino]-3-cyano-5,6-dimethoxybenzo[b]thiophene (4j)

![Chemical structure of 2-[(2-Chlorophenyl)amino]-3-cyano-5,6-dimethoxybenzo[b]thiophene (4j)]

**Reaction Time:** 1h.  
**Yield:** 55%  
**Melting Point:** 186-189 °C.  
**R<sub>f</sub>** = 0.36 in 30% ethyl acetate in hexanes.  

IR (KBr): ν (cm<sup>-1</sup>) = 3791, 3313, 2924, 2854, 2214, 1594, 1498, 1274, 1256, 1212, 1032.  

<sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ = 7.54 (d, J = 7.7 Hz, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.28 (t, J = 7.7 Hz, 1H), 7.17 (s, 1H), 7.11 (s, 1H), 7.08 (s, 1H), 7.04 (t, J = 7.7 Hz, 1H), 3.96 (s, 3H), 3.92 (s, 3H).  

<sup>13</sup>C NMR (175 MHz, CDCl<sub>3</sub>) δ = 155.7, 149.5, 148.1, 137.4, 130.1, 129.4, 128.0, 124.1, 123.5, 122.3, 117.7, 114.7, 104.3, 102.5, 89.1, 56.4, 56.3.  

HR-MS (ESI) Calcd. for C<sub>17</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>2</sub>S [M+H]: 345.0459, Found: 345.0452;  
3-Cyano-2-((3,5-dimethylphenyl)amino)-5,6-dimethoxybenzo[\textit{b}]thiophene (4k)

\[ \text{Reaction Time: 1 h} \]
\[ \text{Yield: 45\%} \]
\[ \text{Melting Point: 168-170 °C.} \]
\[ R_f = 0.30 \text{ in 20\% ethyl acetate in hexanes} \]

IR (KBr): $\nu (\text{cm}^{-1}) = 3658, 3294, 2938, 2197, 2063, 1561, 1491, 1288, 1035.$

$^1$H NMR (700 MHz, CDCl$_3$) $\delta = 7.05$ (s, 1H), 7.04 (s, 1H), 6.96 (brs, 1H), 6.92 (s, 2H), 6.80 (s, 1H), 3.96 (s, 3H), 3.90 (s, 3H), 2.33 (s, 6H).

$^{13}$C NMR (175 MHz, CDCl$_3$) $\delta = 158.9, 149.4, 147.5, 140.2, 139.8, 129.8, 126.5, 121.0, 117.2, 115.6, 104.6, 102.3, 84.5, 56.5, 56.3, 21.5.$

HR-MS (ESI) Calcd for C$_{19}$H$_{18}$N$_2$O$_2$S [M+H]: 339.1162, Found: 339.1153

3-Cyano-2-[(2-(trifluoromethyl)phenyl)amino]-5,6,7-trimethoxybenzo[\textit{b}]thiophene (4l)

\[ \text{Reaction Time: 1h} \]
\[ \text{Yield: 61\%} \]
\[ \text{Melting Point: 134-137 °C.} \]
\[ R_f = 0.30 \text{ in 20\% ethyl acetate in hexanes} \]

IR (KBr): $\nu (\text{cm}^{-1}) = 3430, 3054, 2982, 2262, 1635, 1457, 1265, 889.$

$^1$H NMR (700 MHz, CDCl$_3$) $\delta = 7.69$ (d, $J = 7.7$ Hz, 1H), 7.67 (d, $J = 7.7$ Hz, 1H), 7.59 (t, $J = 7.7$ Hz, 1H), 7.29 (t, $J = 7.7$ Hz, 1H), 7.02 (s, 1H), 6.89 (s, 1H), 4.02 (s, 3H), 3.94 (s, 3H), 3.88 (s, 3H).

$^{13}$C NMR (175 MHz, CDCl$_3$) $\delta = 159.2, 154.4, 147.2, 138.8, 138.5, 133.4, 132.3, 127.2 (q, J = 5.2$ Hz), 125.1, 123.9 (q, $J = 271.3$ Hz), 122.5, 121.9 (q, $J = 29.8$ Hz), 115.2, 114.3, 98.2, 88.0, 61.5, 60.9, 56.4.

HR-MS (ESI) Calcd. for C$_{19}$H$_{15}$F$_3$N$_2$O$_3$S [M+Na]: 431.0648, Found: 431.0650
3-Cyano-2-[(4-fluorophenyl)amino]-5,6,7-trimethoxybenzo[b]thiophene (4m)

![Chemical structure](image)

**Reaction Time:** 1h

**Yield:** 58%

**Melting Point:** 174-177 °C.

**Rf** = 0.23 in 15% in ethyl acetate in hexanes

**IR (KBr):** 3454, 3258, 2920, 2211, 1511, 1115, 825

**1H NMR (700 MHz, CDCl₃)** δ = 7.33-7.31 (m, 3H), 7.10 (t, J = 8.4 Hz, 2H), 6.81 (s, 1H), 4.01 (s, 3H), 3.93 (s, 3H), 3.87 (s, 3H).

**13C NMR (175 MHz, CDCl₃)** δ = 161.7, 160.3 (d, J = 243.25 Hz), 154.3, 147.3, 138.3, 136.3 (d, J = 3.5 Hz), 132.6, 123.1 (d, J = 8.8 Hz), 116.7 (d, J = 22.8 Hz), 115.6, 113.9, 97.8, 83.8, 61.5, 61.0, 56.5.

**HR-MS (ESI) Calcd for C₁₈H₁₅FN₂O₃ [M+Na]:** 381.0680, Found: 381.0665

3-Cyano-2-[(3,5-dimethylphenyl)amino]-5,6-methylenedioxybenzo[b]thiophene (4n)

**Reaction Time:** 1 h

**Yield:** 45%

**Melting Point:** 197-200 °C.

**Rf** = 0.22 in 10% ethyl acetate in hexanes

**IR (KBr):** 3649, 3503, 3447, 2373, 2249, 1830, 1772, 1560, 939, 828, 760

**1H NMR (300 MHz, DMSO)** δ = 9.87 (s, 1H), 7.41 (s, 1H), 6.98 (s, 1H), 6.95 (s, 2H) 6.73 (s, 1H), 6.06 (s, 2H), 2.25 (s, 6H).

**13C NMR (75 MHz, DMSO)** δ = 158.9, 147.1, 145.0, 141.2, 138.5, 130.7, 125.2, 121.2, 117.0, 114.8, 102.6, 101.3, 98.7, 84.1, 20.9.

**HR-MS (ESI) Calcd for C₁₈H₁₄N₂O₂S [M+H]:** 323.0849, Found: 323.0858
3-Cyano-5,6-methylenedioxy-2-[(3-methylphenyl)amino]benzo[b]thiophene (4o)

Reaction Time: 1.5 h
Yield: 45%
Melting Point: 201-203 °C.
Rf = 0.36 in 10% ethyl acetate in hexanes

IR (KBr): ν (cm⁻¹) = 3242, 2921, 2205, 1563, 1473, 1294, 1221, 1039.

¹H NMR (700 MHz, CDCl₃) δ = 7.25-7.21 (m, 1H), 7.13 (brs, 1H), 7.09 (s, 1H), 7.07 (s, 1H), 7.00 (s, 1H), 6.97-6.92 (m, 2H), 5.97 (s, 2H), 2.35 (s, 3H).

¹³C NMR (175 MHz, CDCl₃) δ = 159.0, 147.8, 145.7, 140.3, 140.0, 130.7, 129.7, 125.5, 121.6, 120.2, 116.5, 115.4, 101.9, 101.6, 100.0, 84.7, 21.6.

HR-MS (ESI) Calcd. For C₁₇H₁₂N₂O₂S [M+H]: 309.0692, Found: 309.0682

3-Cyano-2-[(4-isopropylphenyl)amino]benzo[b]thiophene (4p)

Reaction Time: 1 h
Yield: 32%
Melting Point: 174-176 °C.
Rf: 0.32 in 15% ethyl acetate in hexanes

IR (KBr): ν (cm⁻¹) = 3773, 3252, 2957, 2394, 2280, 1605, 1552, 1514, 1439, 1324.

¹H NMR (700 MHz, CDCl₃) δ = 7.59 (d, J = 7.7 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.38 (t, J = 8.4 Hz, 1H), 7.28 – 7.26 (m, 5H), 7.10 (t, J = 7.7 Hz, 1H), 2.85 - 2.81 (m, 1H), 1.17 (d, J = 7.0 Hz, 6H)

¹³C NMR (100 MHz, CDCl₃) δ = 161.5, 146.3, 137.8, 136.8, 129.0, 127.8, 126.1, 123.5, 121.9, 120.8, 119.7, 115.6, 82.7, 33.8, 24.1.

HR-MS (ESI) Calcd for C₁₈H₁₆N₂S [M+Na]: 315.0926, Found: 315.0928

[M+H]: 293.1107, Found: 293.1113
3-Cyano-2-(3-methoxyphenylamino)benzo[b]thiophene (4q)

![Chemical Structure](image1)

Reaction Time: 2 h

Yield: 19%

Rf: 0.38 in 15% ethyl acetate in hexanes

$^1$H NMR (400 MHz, CDCl$_3$) δ = 7.63 (d, $J$ = 8.0 Hz, 1H), 7.60 (d, $J$ = 8.0 Hz, 1H), 7.42 (t, $J$ = 7.2 Hz, 1H), 7.36 - 7.24 (m, 3H), 6.99 – 6.90 (m, 2H), 6.77 (d, $J$ = 8.4 Hz, 1H), 3.87 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 161.0, 160.1, 141.2, 136.5, 130.7, 129.5, 126.2, 123.9, 122.0, 120.0, 115.22, 112.3, 110.7, 105.9, 84.4, 55.6.

HR-MS (ESI) Calcd for C$_{16}$H$_{12}$N$_2$OS [M+H]: 281.0743, Found: 281.0834

2-(5-Methoxybenzo[d]thiazol-2-yl)-2-phenylacetonitrile (4q’)

![Chemical Structure](image2)

Reaction Time: 2 h

Yield: 20%

Rf: 0.35 in 15% ethyl acetate in hexanes

$^1$H NMR (400 MHz, CDCl$_3$) δ = (Mixture of 3-isomers 1: 0.15 : 0.1)7.67 (d, $J$ = 8.8 Hz, 1H), 7.60 - 7.52 (m, 3H), 7.48 - 7.38 (m, 3H), 7.06 (dd, $J$ = 8.8, 2.0 Hz, 1H), 5.63 (s, 1H), 3.88 (s, 3H). (Major Isomer only)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 165.7, 159.4, 153.8, 132.9, 129.6, 129.3, 129.1, 127.9, 121.9, 116., 110.6, 105.8, 55.6, 41.9. (Major Isomer only)

HR-MS (ESI) Calcd for C$_{16}$H$_{12}$N$_2$OS [M+H]: 281.0743, Found: 281.0920

2-(5-Methoxybenzo[d]thiazol-2-yl)-2-(3-(trifluoromethyl)phenyl)acetonitrile(4r’)

![Chemical Structure](image3)

Reaction Time: 2 h

Yield: 22% (Along with other isomers)

Rf: 0.40 in 20% ethyl acetate in hexanes

SI-21
$^1$H NMR (400 MHz, CDCl$_3$) δ = 7.83 - 7.76 (m, 2H), 7.74 – 7.66 (m, 2H), 7.62 - 7.53 (m, 1H), 7.57 - 7.53(m, 1H), 7.11 - 7.06 (m, 1H), 5.69 (s, 1H), 3.89 (s, 3H). (Major Isomer only)

$^{13}$C NMR (100 MHz, CDCl$_3$) was very complicated. However, the characteristic peak of benzo[b]thiophene was not found in the spectrum (80 ppm).

HR-MS (ESI) Calcd for C$_{17}$H$_{11}$F$_3$N$_2$O$^+$ [M+H]: 349.0617, Found: 349.0792

Scheme S2: General Procedure for the Synthesis of Thioamides 5

To a stirring suspension of NaH (60% suspension in mineral oil) (1.2 equiv.) in DMF (10.0 mL) at 0 °C was added dropwise the corresponding benzylnitrile (1 equiv.) in DMF (5.0 mL). After being further stirred for 1 h at room temperature, a solution of alkyl isothiocyanate (1.1 equiv.) in DMF (5.0 mL) was added to the reaction mixture at 0 °C and followed by further stirring for 0.5 – 1 h at room temperature. After complete consumption of the starting materials (monitored by TLC), the reaction mixture was quenched with saturated NH$_4$Cl solution and extracted with EtOAc. The combined organic layer washed with water (3 x 25 mL) & brine (25 mL), dried over anhyd. Na$_2$SO$_4$ and concentrated under reduced pressure. The crude products were purified by flash chromatography using EtOAc/hexanes as eluent.

2-Cyano-2-(3,4-methylenedioxyphenyl)-N-cyclohexylethanethioamide (5a)

Reaction Time: 3 h
Yield: 98%, yellow colour solid
Melting Point: 139-140 °C.

Rf: 0.32 in 40% ethyl acetate in hexanes

IR (KBr): 3279, 2853, 2929, 2199, 1560, 1108, 743.
\( ^1 \)H NMR (300 MHz, CDCl\(_3\)) \( \delta = 7.31 \text{ (s, 1H)}, 6.95 - 6.86 \text{ (m, 2H)}, 6.85 - 6.77 \text{ (m, 1H)}, 6.01 \text{ (s, 2H)}, 5.05 \text{ (s, 1H)}, 4.36 - 4.16 \text{ (m, 1H)}, 2.10 - 1.90 \text{ (m, 2H)}, 1.75 - 1.55 \text{ (m, 3H)}, 1.45 - 1.30 \text{ (m, 2H)}, 1.30 - 1.10 \text{ (m, 3H)}. \\

\( ^{13} \)C NMR (175 MHz, CDCl\(_3\)) \( \delta = 191.2, 148.6, 125.4, 121.7, 117.5, 108.9, 108.0, 101.8, 55.1, 52.9, 30.9, 30.9, 25.3, 24.5. \\

HR-MS (ESI) Calcd for C\(_{16}\)H\(_{18}\)N\(_2\)O\(_2\)S [M+H]: 303.1162, Found: 303.0963

2-Cyano-N-cyclohexyl-2-phenylethanethioamide (5b)

![Chemical structure](attachment:structure.png)

Reaction Time: 3 h
Yield: 64%, yellow colour solid
Melting Point: 93-94%

Rf: 0.38 in 25% ethyl acetate in hexane

IR (KBr): 3282, 2936, 2249, 1537, 1437, 1070

\( ^1 \)H NMR (700 MHz, CDCl\(_3\)) \( \delta = 7.49 - 7.45 \text{ (m, 2H)}, 7.45 - 7.39 \text{ (m, 4H)}, 5.18 \text{ (s, 1H)}, 4.30 - 4.21 \text{ (m, 1H)}, 2.02 - 1.90 \text{ (m, 2H)}, 1.69 - 1.56 \text{ (m, 3H)}, 1.41 - 1.29 \text{ (m, 2H)}, 1.28 - 1.12 \text{ (m, 3H)}. \\

\( ^{13} \)C NMR (75 MHz, CDCl\(_3\)) \( \delta = 191.6, 132.5, 129.9, 129.8, 128.1, 118.1, 55.6, 53.6, 31.2, 31.1, 25.6, 24.8. \\

HR-MS (ESI) Calcd for C\(_{15}\)H\(_{18}\)N\(_2\)S [M+H]: 259.1263, Found: 259.1098

[M+Na]: 281.1083, Found: 281.1063

2-Cyano-N-ethyl-2-(3,4-methylenedioxyphenyl)ethanethioamide (5c)

![Chemical structure](attachment:structure.png)

Reaction Time: 3 h
Yield: 89%, pale yellow colour liquid

Rf: 0.30 in 10% ethyl acetate in hexanes

IR (KBr): 3445, 3012, 2915, 2362, 2236, 1652, 1539, 1488, 1275, 1032, 764.

\( ^1 \)H NMR (700 MHz, CDCl\(_3\)) \( \delta = 7.59 \text{ (s, 1H)}, 6.96 - 6.92 \text{ (m, 2H)}, 6.83 \text{ (d, } J = 8.4 \text{ Hz, 1H)}, 6.00 \text{ (s, 2H)}, 5.10 \text{ (s, 1H)}, 3.70 - 3.58 \text{ (m, 2H)}, 1.22 \text{ (t, } J = 7.7 \text{ Hz, 3H}). \\

SI-23
$^{13}$C NMR (175 MHz, CDCl$_3$) $\delta =$ 192.7, 148.6, 148.5, 125.3, 121.8, 117.7, 108.8, 108.0, 101.7, 52.5, 41.8, 12.6.

HR-MS (ESI) Calcd for C$_{12}$H$_{12}$N$_2$O$_2$S [M+Na]: 271.0512, Found: 271.0481

2-Cyano-N-ethyl-2-(4-methoxyphenyl)ethanethioamide (5d)

Reaction Time: 3 h
Yield: 91%, pale yellow colour liquid
R$_f$: 0.34 in 40% ethyl acetate in hexanes

IR (KBr): 3445, 3006, 2360, 2270, 2341, 1559, 1275, 764.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 7.79 (s, 1H), 7.31 (t, $J = 8.0$ Hz, 1H), 7.08-7.00 (m, 2H), 6.94-6.89 (m, 1H), 5.18 (s, 1H), 3.79 (s, 3H), 3.66 – 3.56 (m, 2H), 1.18 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (75 MHz, DMSO) $\delta =$ 192.7, 159.4, 135.1, 130.0, 119.7, 118.1, 113.7, 113.6, 55.2, 50.8, 41.0, 12.4.

HR-MS (ESI) Calcd for C$_{12}$H$_{14}$N$_2$OS [M+H]: 235.0900, Found: 235.0850

2-Cyano-2-(3,4-dimethoxyphenyl)-N-(4-methoxybenzyl)ethanethioamide (5e)

Reaction Time: 3 h
Yield: 63%, yellow colour solid
Melting Point: 127-128 ºC.

R$_f$: 0.32 in 40% ethyl acetate in hexanes

IR (KBr): 3270, 2249, 1574, 1262, 1019

$^1$H NMR (700 MHz, CDCl$_3$) $\delta =$ 7.75 (s, 1H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.98 (dd, $J = 6.3$, 2.1 Hz, 1H), 6.93 (d, $J = 2.1$ Hz, 1H), 6.84 (d, $J = 8.4$ Hz, 1H), 6.81 (d, $J = 7.7$ Hz, 2H), 5.15 (s, 1H), 4.70 (d, $J = 4.9$ Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 3.76 (s, 3H).

$^{13}$C NMR (175 MHz, CDCl$_3$) $\delta =$ 193.0, 159.4, 149.8, 149.5, 129.4, 127.3, 123.9, 120.5, 117.6, 114.2, 111.5, 110.5, 56.0, 55.9, 55.2, 52.5, 50.0.

HR-MS (ESI) Calcd for C$_{19}$H$_{20}$N$_2$O$_3$S [M+H]: 357.1267, Found: 357.1276
2-Cyano-N-(4-methoxybenzyl)-2-(4-methylphenyl)ethanethioamide (5f)

Reaction Time: 3 h
Yield: 61%
Melting Point: 104-106 °C.

Rf: 0.36 in 25% in ethyl acetate in hexanes

IR (KBr): 3334, 2952, 2058, 1537, 1512, 1249, 1231, 1129, 1033, 815, 662

$^1$H NMR (700 MHz, CDCl$_3$) $\delta = 7.55$ (s, 1H), 7.34 (d, $J = 7.7$ Hz, 2H), 7.22 (d, $J = 7.7$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 6.85 (d, $J = 7.0$ Hz, 2H), 5.17 (s, 1H), 4.70 (d, $J = 4.9$ Hz, 2H), 3.79 (s, 3H), 2.36 (s, 3H)

$^{13}$C NMR (175 MHz, CDCl$_3$) $\delta = 192.8$, 159.7, 139.8, 130.4, 129.5, 128.8, 127.8, 127.2, 117.3, 114.5, 55.4, 53.0, 50.5, 21.3

HR-MS (ESI) Calcd for C$_{18}$H$_{16}$N$_2$S [M+H]: 311.1213, found: 311.1209

2-Cyano-N-(4-methoxybenzyl)-2-phenylethanethioamide (5g)

Reaction Time: 3 h
Yield: 80%, brown colour solid
Melting Point: 99-100 °C.

Rf: 0.30 in 30% ethyl acetate in hexanes

IR (KBr): $\nu$ (cm$^{-1}$) = 3260, 2938, 2835, 2249, 1600, 1508, 1438, 1250, 1035, 1019.

$^1$H NMR (700 MHz, CDCl$_3$) $\delta = 7.86$ (s, 1H), 7.51 – 7.44 (m, 2H), 7.43 – 7.37 (m, 3H), 7.12 (d, $J = 9.1$ Hz, 2H), 6.87 – 6.79 (m, 2H), 5.20 (s, 1H), 4.69 (d, $J = 4.9$ Hz, 2H), 3.77 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 192.6$, 159.6, 131.8, 129.6, 129.6, 129.5, 127.8, 127.2, 117.3, 114.4, 55.4, 53.1, 50.3

HR-MS (ESI) Calcd for C$_{17}$H$_{16}$N$_2$S [M+Na]: 319.0876, Found: 319.0858
General Procedure for Site Selective C–S Bond Formation of sp² C–H bond vs sp³ C–H bond

An oven-dried 8 mL reaction vial was charged with NiBr₂ (2 mol%), Ad₂PBU (4 mol%), PIDA (0.5 mmol), and KI (1 mmol), respective thioamide 5 (0.5 mmol) in HFIP (2.0 mL), was stirred at 50 °C for 1-1.5 h. The reaction mixture was monitored by TLC. After the starting material had been completely consumed, the reaction mixture was purified by flash chromatography.

3-Cyano-2-(cyclohexylamino)-5,6-methylenedioxybenzo[b]thiophene (6a)

Reaction Time: 1 h
Yield: 50%
Melting Point: 161-163 °C.
R_f: 0.25 in 10 % ethyl acetate in hexanes

IR (KBr): 3555, 2846, 2243, 2065, 1635, 1556, 1472, 1260, 749

^1^H NMR (300 MHz, DMSO) δ = 7.98 (d, J = 7.8 Hz, 1H), 7.32 (s, 1H), 6.80 (s, 1H), 6.01 (s, 2H), 2.05-1.90 (m, 2H), 1.81-1.68 (m, 2H), 1.67-1.52 (m, 1H), 1.40-1.09 (m, 6H).

^1^C NMR (175 MHz, CDCl₃) δ = 163.4, 147.5, 144.5, 131.8, 120.3, 116.2, 102.0, 101.3, 99.6, 78.4, 57.2, 33.3, 25.3, 24.8.

HR-MS (ESI) Calcd for C₁₆H₁₆N₂O₂S [M+H]: 301.1005, Found: 301.1001
3-Cyano-2-(cyclohexylamino)benzo[b]thiophene (6b)

Reaction Time: 1 h
Yield: 68%
Melting Point: 132-134% ºC.
Rf: 0.24 in 10% ethyl acetate in hexanes

IR (KBr): ν (cm⁻¹) = 3280, 2926, 2852, 2200, 1566, 1364, 1107, 743.

¹H NMR (400 MHz, CDCl₃) δ = 7.53-7.48 (m, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H), 5.23 (s, 1H), 3.40-3.20 (m, 1H), 2.25-2.05 (m, 2H), 1.95-1.75 (m, 2H), 1.74-1.60 (m, 1H), 1.50-1.15 (m, 5H)

¹³C NMR (100 MHz, CDCl₃) δ = 164.3, 137.8, 128.6, 126.0, 122.4, 121.8, 119.2, 116.2, 78.1, 57.4, 33.3, 25.4, 24.8.

HR-MS (ESI) Calcd for C₁₅H₁₆N₂S [M+H]: 257.1107, Found: 257.1101

3-Cyano-2-(ethylamino)-5,6-methylenedioxybenzo[b]thiophene (6c)

Reaction Time: 1 h
Yield: 33%, white colour solid
Melting Point: 195 ºC. decomposed

Rf: 0.29 in 10% ethyl acetate in hexanes

IR (KBr): 3218, 2197, 1573, 1103

¹H NMR (300 MHz, DMSO) δ = 8.03 (s, 1H), 7.33 (s, 1H), 6.82 (s, 1H), 6.01 (s, 2H), 3.41-3.20 (m, 2H), 1.40-1.05 (m, 3H)

¹³C NMR (75 MHz, DMSO) δ = 164.0, 146.9, 143.7, 132.1, 119.3, 116.1, 102.6, 101.0, 98.1, 75.4, 41.5, 14.2.

HR-MS (ESI) Calcd for C₁₂H₁₀N₂O₂S [M+H]: 247.0536, Found: 247.0531
3-Cyano-2-(ethylamino)-6-methoxybenzo[b]thiophene (6d)

![Chemical Structure]

Reaction Time: 1h
Yield: 40%, yellow colour solid
Melting Point: 130-131 ºC.

Rf: 0.38 in 20% ethyl acetate in hexanes

IR (KBr): 3284, 2203, 1574, 1095.

$^1$H NMR (700 MHz, CDCl$_3$) \( \delta = 7.39 \) (d, \( J = 8.4 \) Hz, 1H), \( 6.99 \) (d, \( J = 2.8 \) Hz, 1H), \( 6.73-6.76 \) (m, 1H), \( 5.30 \) (s, 1H), \( 3.85 \) (s, 3H), \( 3.38 \) (q, \( J = 7.0 \) Hz, 2H), \( 1.36 \) (t, \( J = 7.0 \) Hz, 3H)

$^{13}$C NMR (175 MHz, CDCl$_3$) \( \delta = 166.5, 159.0, 139.1, 122.6, 120.2, 116.3, 111.5, 102.7, 78.1, 55.7, 42.5, 14.8 \).

HR-MS (ESI) Calcd for C$_{12}$H$_{12}$N$_2$OS [M+H]: 233.0743, Found: 233.0724

3-Cyano-5,6-dimethoxy-2-[(4-methoxybenzyl)amino]benzo[b]thiophene (6e)

![Chemical Structure]

Reaction Time: 1 h
Yield: 37%, white colour solid
Melting Point: 157-159 ºC.

Rf: 0.23 in 20% ethyl acetate in hexanes

IR (KBr): 3249, 2206, 1491, 1250, 1027

$^1$H NMR (700 MHz, CDCl$_3$) \( \delta = 7.30 \) (d, \( J = 8.4 \) Hz, 2H), \( 7.01 \) (s, 1H), \( 6.98 \) (s, 1H), \( 6.90 \) (d, \( J = 8.4 \) Hz, 2H), \( 4.42 \) (s, 2H), \( 3.93 \) (s, 3H), \( 3.87 \) (s, 3H), \( 3.81 \) (s, 3H)

$^{13}$C NMR (75 MHz, DMSO) \( \delta = 164.2, 158.6, 148.8, 145.8, 130.7, 129.6, 128.8, 119.1, 116.3, 113.9, 106.0, 101.1, 76.0, 56.0, 55.6, 55.1, 49.3 \).

HR-MS (ESI) Calcd for C$_{19}$H$_{18}$N$_2$O$_3$S [M+Na]: 377.0930, Found: 377.0918
3-Cyano-2-[(4-methoxyphenyl)amino]-6-methylbenzo[b]thiophene (6f)

Reaction Time: 1 h
Yield: 51%
Melting Point: 108-110 °C
Rf: 0.30 in 20% ethyl acetate in hexanes

IR (KBr): 3430, 3271, 2363, 2198, 1598, 1567, 1262, 1167, 1027, 814

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.41$ (d, $J = 8.0$ Hz, 1H), 7.34 (s, 1H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 2H), 5.47 (s, 1H), 4.45 (s, 2H), 3.82 (s, 3H), 2.40 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 164.4$, 159.7, 135.1, 132.5, 129.2, 129.0, 128.4, 127.4, 122.0, 119.1, 116.2, 114.4, 78.7, 55.4, 51.0, 21.4.

HR-MS (ESI) Calcd for C$_{18}$H$_{16}$N$_2$O$_2$ [M+Na]: 331.0876, found: 331.0894

3-Cyano-2-[(4-methoxybenzyl)amino]benzo[b]thiophene (6g)

Reaction Time: 1 h
Yield: 35%, light orange colour solid
Melting Point: 134-136 °C.

Rf: 0.29 in 10% ethyl acetate in hexanes

IR (KBr): 3301, 2196, 1570, 1248, 1035

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.52$ (t, $J = 6.8$ Hz, 2H), 7.34 (t, $J = 7.2$ Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.14 (t, $J = 7.2$ Hz, 1H), 6.92 (d, $J = 8.8$ Hz, 2H), 5.68 (s, 1H), 4.47 (s, 2H), 3.82 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 164.9$, 159.8, 137.7, 129.3, 128.8, 128.3, 126.2, 122.7, 122.0, 119.5, 116.0, 114.5, 79.0, 55.5, 51.1.

HR-MS (ESI) Calcd for C$_{17}$H$_{14}$N$_2$O$_2$ [M+Na]: 317.0719, Found: 317.0705
Scheme S3: Controlled Experiments

The controlled experiments clearly show that the electronic factor was partly influenced for site selective C—S bond formation.

Scheme S4: A Plausible Mechanism for Nickel Catalyzed C—H Bond Functionalization

Crystal Data

Crystallographic data of 4a in CH$_2$Cl$_2$/n-hexane: C$_{17}$H$_{14}$N$_2$O$_2$S, Mw = 310.38, monoclinic, space group P2$_1$/c, a = 11.7047 (2) Å, b = 10.3186 (2) Å, c = 13.6857 (2) Å, α = 90°, β = 113.046 (2) °, γ = 90°, V = 1520.99 (6) Å$^3$, Z = 4, Dcalc = 1.355 mg/m$^3$, T = 293 K, R1 = 0.0443 \{I > 2σ(I)\}, wR2 = 0.1241, GOF = 1.056.
Crystallographic data of 4b in CH₂Cl₂/n-hexane: C₁₇H₁₄N₂O₂S, Mw = 310.36, orthorhombic, space group Pbca, a = 14.4456 (3) Å, b = 9.07642 (17) Å, c = 22.7259 (5) Å, α = 90°, β = 90°, γ = 90°, V = 12979.69 (11) Å³, Z = 8, Dcalc = 1.384 mg/m³, T = 293 K, R1 = 0.0930{I > 2σ (I)}, wR2 = 0.2464, GOF = 1.165.

References:
$^1$H NMR Spectrum of 3a in CDCl$_3$ at 300 MHz

$^{13}$C NMR of Spectrum of 3a in CDCl$_3$ at 175 MHz
$^1$H-NMR Spectrum of 3b in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3b in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3c in CDCl$_3$ at 300 MHz

$^{13}$C NMR Spectrum of 3c in CDCl$_3$ at 75 MHz
$^1$H NMR Spectrum of 3d in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3d in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3e in DMSO at 300 MHz

$^{13}$C NMR Spectrum of 3e in DMSO at 75 MHz
$^1$H NMR Spectrum of 3f in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3f in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3g in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 3g in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 3h$^1$ in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3h$^1$ in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 3i in DMSO at 300 MHz

$^{13}$C NMR Spectrum of 3i in CDCl$_3$ at 175 MHz
$^{1}H$ NMR Spectrum of 3j in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3j in CDCl$_3$ at 75 MHz
$^1$H NMR Spectrum of 3k in DMSO at 700 MHz

$^{13}$C NMR Spectrum of 3k in DMSO at 175 MHz
$^{1}H$ NMR Spectrum of 3l in CDCl$_3$ at 400 MHz

$^{13}C$ NMR Spectrum of 3l in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 3m in CDCl$_3$ at 300 MHz

$^{13}$C NMR Spectrum of 3m in CDCl$_3$ at 75 MHz
$^1$H NMR Spectrum of 3n in CDCl$_3$ at 300 MHz

$^{13}$C NMR Spectrum of 3n in CDCl$_3$ at 75 MHz
$^1$H NMR Spectrum of 3o in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3o in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 3p in DMSO at 700 MHz

$^{13}$C NMR Spectrum of 3p in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 3q in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3q in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3r in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3r in CDCl$_3$ at 100 MHz
$^1$H NMR spectrum of 4a in DMSO at 700 MHz

$^{13}$C NMR Spectrum of 4a in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 4b in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 4b in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 4c in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 4c in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 4d in DMSO at 400 MHz

$^{13}$C NMR Spectrum of 4d in DMSO at 100 MHz
$^1$H NMR Spectrum of 4e in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 4e in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 4f in DMSO at 700 MHz

$^{13}$C NMR Spectrum of 4f in DMSO at 100 MHz
$^1$H NMR Spectrum of 4g in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 4g in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 4h$^2$ in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 4h$^2$ in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 4i in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 4i in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 4j in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 4j in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 4k in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 4k in CDCl$_3$ at 175 MHz
\(^1\)H NMR Spectrum of 4l in CDCl\(_3\) at 700 MHz

\(^{13}\)C NMR Spectrum of 4l in CDCl\(_3\) at 175 MHz
$^1$H NMR Spectrum of 4m in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 4m in CDCl$_3$ at 175 MHz
\(^1\)H NMR Spectrum of 4n in DMSO at 300 MHz

\(^{13}\)C NMR Spectrum of 4n in DMSO at 75 MHz
$^1$H NMR Spectrum of 4o in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 4o in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 4p in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 4p in CDCl$_3$ at 100 MHz
\(^1\)H NMR Spectrum of 4q in CDCl\(_3\) at 400 MHz

\(^{13}\)C NMR Spectrum of 4q in CDCl\(_3\) at 100 MHz
$^1$H NMR Spectrum of 4q’ in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 4q’ in CDCl$_3$ at 100 MHz
\(^1\)H NMR Spectrum of 4r’ & 4r” in CDCl\(_3\) at 400 MHz

\(^{13}\)C NMR Spectrum of 4r’ & 4r” in CDCl\(_3\) at 100 MHz

It is very complicated spectrum, in \(^{13}\)C spectrum absence of peak at 80 ppm indicates that no formation of benzo[\(b\)]thiophene.
$^1$H NMR Spectrum of 5a in CDCl$_3$ at 300 MHz

$^{13}$C NMR Spectrum of 5a in CDCl$_3$ at 75 MHz
$^1$H NMR Spectrum of 5b$^2$ in CDCl$_3$ at 700 MHz

13C NMR Spectrum of 5b$^2$ in CDCl$_3$ at 75 MHz
$^1$H NMR Spectrum of 5c in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 5c in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 5d in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 5d in DMSO at 75 MHz
$^1$H NMR Spectrum of 5e in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 5e in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 5f in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 5f in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 5g in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 5g in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 6a in DMSO at 300 MHz

$^{13}$C NMR Spectrum of 6a in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 6b in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 6b in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 6c in DMSO at 300 MHz

$^{13}$C NMR Spectrum of 6c in DMSO at 75 MHz
$^1$H NMR Spectrum of 6d in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 6d in CDCl$_3$ at 175 MHz
$^1$H NMR Spectrum of 6e in CDCl$_3$ at 700 MHz

$^{13}$C NMR Spectrum of 6e in DMSO at 75 MHz
$^1$H NMR Spectrum of 6f in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 6f in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 6g in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 6g in CDCl$_3$ at 100 MHz
HR-MS Spectrum of 3a

HR-MS Spectrum of 3b

HR-MS Spectrum of 3c
HR-MS Spectrum of 3g

HR-MS Spectrum of 3h

HR-MS Spectrum of 3i
HR-MS Spectrum of 3j

HR-MS Spectrum of 3k

HR-MS Spectrum of 3l
HR-MS Spectrum of 3p

HR-MS Spectrum for 3q

HR-MS Spectrum for 3r
HR-MS Spectrum of 4a

HR-MS Spectrum of 4c

HR-MS Spectrum of 4d
HR-MS Spectrum of 4e

HR-MS Spectrum of 4f

HR-MS Spectrum of 4g
HR-MS Spectrum of 4k

[Graph showing mass spectrum with peaks at 339.1153, 339.3375, 340.1176, and 341.1148. Molecular structure with chemical formula C19H18N2O2S, M+H 339.12.

HR-MS Spectrum of 4l

[Graph showing mass spectrum with peaks at 431.0650, 432.0681, and 433.0608. Molecular structure with chemical formula C19H15F3N2O3S, M+Na 431.07.

HR-MS Spectrum of 4m

[Graph showing mass spectrum with peaks at 381.0665, 382.0682, 383.0647, and 361.0660. Molecular structure with chemical formula C18H15F2N2O3S, M+Na 381.07.

SI-92
HR-MS Spectrum of 4r’

HR-MS Spectrum of 5a

HR-MS Spectrum of 5b
(M+nNa)
HR-MS Spectrum of 6d

HR-MS Spectrum of 6e

HR-MS Spectrum of 6f
HR-MS Spectrum of 6g