

Supporting Information

Copper-Catalyzed Domino Synthesis of Benzo[*b*]thiophene/Imidazo[1,2-*a*]pyridines by Sequential Ullmann-Type Coupling and Intramolecular C(sp²)-H Thiolation

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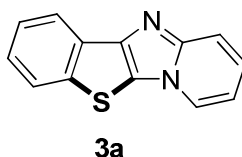
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General information and materials

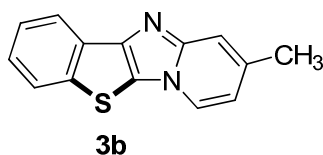
^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 with TMS as internal standard (400 MHz ^1H , 100 MHz ^{13}C) at room temperature. All commercially available reagent and chemicals were purchased from chemical suppliers and used as received without further purification. Column chromatography was performed on silica gel (200-300 mesh). Mass analyses and HRMS were obtained by ESI on a TOF mass analyzer.

General procedure for synthesis of compounds 3a-3u and 3a-3u:

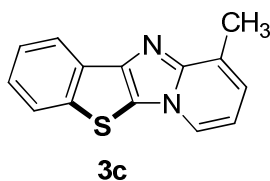
A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with substituted 2-(2-bromophenyl)imidazo[1,2-*a*]pyridines (**1**) (0.3 mmol), K_2S (0.6 mmol), CuI (0.03 mmol), 1,10-Phen (0.03 mmol), and DMF (2 mL). Then the mixture was allowed to stir under air atmosphere at 120°C for 24 h. After completion of the reaction, the resulting solution was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product.



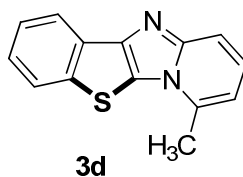
Compound **3a**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.28 (d, 1H, $J = 8.0$ Hz), 8.13 (d, 1H, $J = 4.0$ Hz), 7.87 (d, 1H, $J = 8.0$ Hz), 7.78 (d, 1H, $J = 8.0$ Hz), 7.53 (t, 1H, $J = 8.0$ Hz), 7.44 (t, 1H, $J = 8.0$ Hz), 7.29-7.26 (m, 1H), 6.92 (t, 1H, $J = 8.0$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 149.5, 145.9, 140.2, 129.1, 125.5, 125.4, 124.4, 124.2, 124.2, 121.7, 118.4, 112.2. HRMS m/z calcd. for $\text{C}_{13}\text{H}_9\text{N}_2\text{S}$ $[\text{M}+\text{H}]^+$: 225.0486, found: 225.0481.



Compound **3b**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.23 (d, 1H, $J = 8.0$ Hz), 7.92 (d, 1H, $J = 8.0$ Hz), 7.82 (d, 1H, $J = 8.0$ Hz), 7.52-7.47 (m, 2H), 7.39 (t, 1H, $J = 8.0$ Hz), 6.67 (d, 1H, $J = 8.0$ Hz), 2.41 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 150.8, 145.6, 140.0, 135.6, 129.1, 125.3, 125.2, 124.2, 123.3, 122.0, 121.5, 116.6, 114.7, 21.6. HRMS m/z calcd. for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{S}$ $[\text{M}+\text{H}]^+$: 239.0643, found: 239.0638.

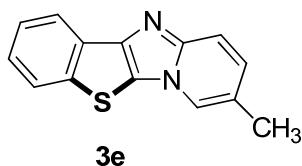


Compound **3c**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.33 (d, 1H, $J = 8.0$ Hz), 7.93 (d, 1H, $J = 8.0$ Hz), 7.83 (d, 1H, $J = 8.0$ Hz), 7.50 (t, 1H, $J = 8.0$ Hz), 7.40 (t, 1H, $J = 8$ Hz), 7.02 (d, 1H, $J = 8.0$ Hz), 6.77 (t, 1H, $J = 8.0$ Hz), 2.73 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 150.0, 145.3, 140.1, 129.2, 128.3, 125.3, 125.2, 124.2, 123.3, 123.1, 122.1, 121.7, 112.1, 17.5. HRMS m/z calcd. for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{S}$ $[\text{M}+\text{H}]^+$: 239.0643, found: 239.0638.

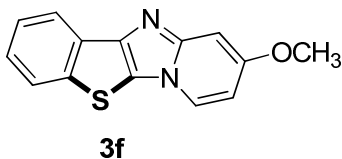


Compound **3d**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.29 (d, 1H, $J = 8.0$ Hz), 7.84 (d, 1H, $J = 8.0$ Hz), 7.62 (d, 1H, $J = 12.0$ Hz), 7.53 (t, 1H, $J = 8.0$ Hz), 7.42 (t, 1H, $J = 8.0$ Hz), 7.17 (t, 1H, $J = 8.0$ Hz), 6.61 (d, 1H, $J = 8.0$ Hz), 2.88 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 150.5, 145.7, 140.8, 134.4, 130.9, 128.6, 125.3, 125.2, 125.2, 123.7, 121.5, 115.7, 110.9, 19.0. HRMS m/z

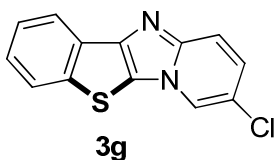
calcd. for C₁₄H₁₁N₂S [M+H]⁺: 239.0643, found: 2239.0638.



Compound **3e**: Eluent petroleum ether/ethyl acetate (5:1). ¹H NMR (CDCl₃, 400 MHz, ppm) δ 8.23 (d, 1H, *J* = 8.0 Hz), 7.82 (d, 2H, *J* = 8 Hz), 7.62 (d, 1H, *J* = 8.0 Hz), 7.49 (t, 1H, *J* = 8.0 Hz), 7.39 (t, 1H, *J* = 8.0 Hz), 7.05 (d, 1H, *J* = 8.0 Hz), 2.33 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 148.6, 145.7, 140.8, 129.1, 127.6, 125.3, 125.3, 124.2, 122.2, 121.9, 121.8, 121.5, 117.5, 18.2. HRMS *m/z* calcd. for C₁₄H₁₁N₂S [M+H]⁺: 239.0643, found: 239.0638.

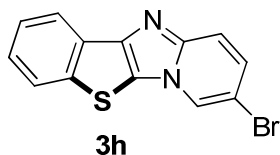


Compound **3f**: Eluent petroleum ether/ethyl acetate (3:1). ¹H NMR (CDCl₃, 400 MHz, ppm) δ 8.22 (d, 1H, *J* = 8.0 Hz), 7.96 (d, 1H, *J* = 8.0 Hz), 7.85 (d, 1H, *J* = 8.0 Hz), 7.51 (t, 1H, *J* = 8.0 Hz), 7.40 (t, 1H, *J* = 8 Hz), 7.04 (s, 1H), 6.66 (d, 1H, *J* = 8.0 Hz), 3.92 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 157.9, 139.8, 129.1, 125.3, 125.0, 124.7, 124.2, 121.3, 107.5, 95.6, 55.6. HRMS *m/z* calcd. for C₁₄H₁₁N₂OS [M+H]⁺: 255.0529, found: 255.0531.

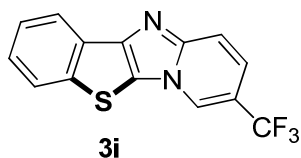


Compound **3g**: Eluent petroleum ether/ethyl acetate (5:1). ¹H NMR (CDCl₃, 400 MHz, ppm) δ 8.24 (d, 1H, *J* = 8.0 Hz), 8.15 (s, 1H), 7.83 (d, 1H, *J* = 8.0 Hz), 7.69 (d, 1H, *J* = 8.0 Hz), 7.52 (t, 1H, *J* = 8 Hz), 7.44 (t, 1H, *J* = 8.0 Hz), 7.21 (d, 1H, *J* = 8.0 Hz).

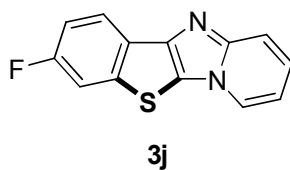
^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 147.8, 146.7, 140.2, 128.7, 125.9, 125.8, 125.6, 124.3, 123.0, 122.0, 121.8, 120.4, 118.6. HRMS m/z calcd. for $\text{C}_{13}\text{H}_8\text{ClN}_2\text{S}$ $[\text{M}+\text{H}]^+$: 259.0097, found: 259.0099.



Compound **3h**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.31 (s, 1H), 8.27 (d, 1H, $J = 8.0$ Hz), 7.88 (d, 1H, $J = 8.0$ Hz), 7.69 (d, 1H, $J = 8.0$ Hz), 7.55 (t, 1H, $J = 8.0$ Hz), 7.47 (t, 1H, $J = 8.0$ Hz), 7.35 (d, 1H, $J = 8.0$ Hz), 6.92 (t, 1H, $J = 8.0$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 147.9, 146.7, 140.3, 128.7, 127.8, 126.0, 125.6, 124.3, 124.2, 121.9, 118.9, 106.7, 100.0. HRMS m/z calcd. for $\text{C}_{13}\text{H}_8\text{BrN}_2\text{S}$ $[\text{M}+\text{H}]^+$: 302.9592, 304.9571, found: 302.9598, 304.9579.

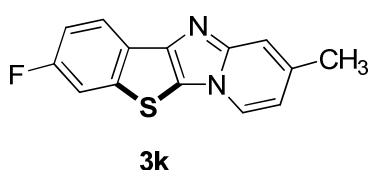


Compound **3i**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.52 (s, 1H), 8.28 (d, 1H, $J = 8.0$ Hz), 7.88 (t, 2H, $J = 8.0$ Hz), 7.56 (t, 1H, $J = 8.0$ Hz), 7.48 (t, 1H, $J = 8$ Hz), 7.43 (d, 1H, $J = 8.0$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 149.1, 147.6, 140.4, 128.6, 126.2, 125.7, 124.3, 123.5 (q, $J_{\text{F-C}} = 352.2$ Hz), 123.2 (q, $J_{\text{F-C}} = 24.3$ Hz), 122.0, 120.0 (q, $J_{\text{F-C}} = 8.1$ Hz), 118.9, 116.5 (q, $J_{\text{F-C}} = 136.0$ Hz). HRMS m/z calcd. for $\text{C}_{14}\text{H}_8\text{F}_3\text{N}_2\text{S}$ $[\text{M}+\text{H}]^+$: 293.0360, found: 293.0351.

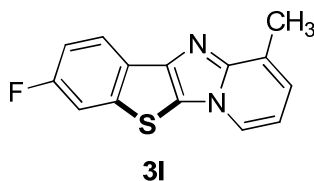


Compound **3j**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz,

ppm) δ 8.19 (q, 1H, $J = 4.0$ Hz), 8.09 (d, 1H, $J = 8.0$ Hz), 7.75 (d, 1H, $J = 8.0$ Hz), 7.55 (d, 1H, $J = 8.0$ Hz), 7.25 (t, 2H, $J = 8.0$ Hz), 6.91 (t, 1H, $J = 8.0$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 162.0, 159.6, 149.6, 145.2, 141.1(d, $J_{\text{F-C}} = 4.0$ Hz), 125.5, 124.5, 124.1, 122.4(d, $J_{\text{F-C}} = 36.2$ Hz), 118.4, 113.7 (d, $J_{\text{F-C}} = 92.1$ Hz), 112.2, 110.8 (d, $J_{\text{F-C}} = 104.0$ Hz). HRMS m/z calcd. for $\text{C}_{13}\text{H}_8\text{FN}_2\text{S}$ $[\text{M}+\text{H}]^+$: 243.0392, found: 243.0397.

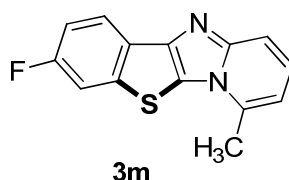


Compound **3k**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.15 (q, 1H, $J = 4.0$ Hz), 7.93 (d, 1H, $J = 8.0$ Hz), 7.52 (d, 1H, $J = 8.0$ Hz), 7.47 (s, 1H), 7.23 (t, 1H, $J = 8.0$ Hz), 6.71 (d, 1H, $J = 8.0$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 161.9, 159.4, 150.0, 144.9, 140.9 (d, $J_{\text{F-C}} = 40.2$ Hz), 135.7, 125.6, 123.2, 122.2 (d, $J_{\text{F-C}} = 36.1$ Hz), 116.7, 114.8, 113.6 (d, $J_{\text{F-C}} = 92.2$ Hz), 110.7 (d, $J_{\text{F-C}} = 104.0$ Hz), 21.6. HRMS m/z calcd. for $\text{C}_{14}\text{H}_{10}\text{FN}_2\text{S}$ $[\text{M}+\text{H}]^+$: 257.0549, found: 257.0557.

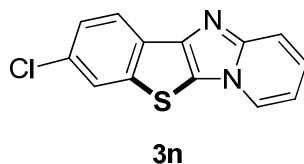


Compound **3l**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.26 (q, 1H, $J = 4.0$ Hz), 7.98 (d, 1H, $J = 8.0$ Hz), 7.56 (d, 1H, $J = 8.0$ Hz), 7.25 (t, 1H, $J = 8.0$ Hz), 7.08 (d, 1H, $J = 8.0$ Hz), 6.85 (t, 1H, $J = 8.0$ Hz), 2.74 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 161.9, 159.8, 150.1, 144.6, 141.0 (d, $J_{\text{F-C}} = 40.1$

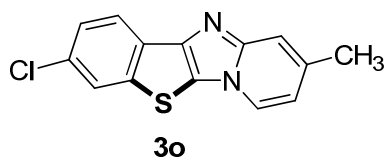
Hz), 128.4, 125.7, 123.4, 122.4 (d, J_{F-C} = 36.1 Hz), 121.9, 113.6 (d, J_{F-C} = 92.2 Hz), 112.2, 110.7 (d, J_{F-C} = 104.2 Hz), 17.4. HRMS m/z calcd. for $C_{14}H_{10}FN_2S$ $[M+H]^+$: 257.0549, found: 257.0557.



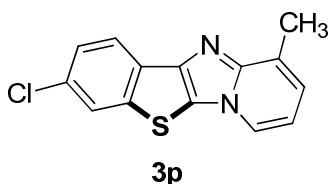
Compound **3m**: Eluent petroleum ether/ethyl acetate (5:1). 1H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.22 (t, 1H, J = 8.0 Hz), 7.61 (d, 1H, J = 8.0 Hz), 7.54 (d, 1H, J = 8.0 Hz), 7.26 (d, 1H, J = 8.0 Hz), 7.20 (t, 1H, J = 8.0 Hz), 6.65 (d, 1H, J = 4.0 Hz), 2.89 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 161.9, 159.5, 141.7 (d, J_{F-C} = 40.2 Hz), 134.3, 125.4, 125.1, 122.3 (d, J_{F-C} = 36.2 Hz), 115.7, 113.6 (d, J_{F-C} = 92.2 Hz), 111.1, 110.2 (d, J_{F-C} = 104.2 Hz), 19.1. HRMS m/z calcd. for $C_{14}H_{10}FN_2S$ $[M+H]^+$: 257.0549, found: 257.0557.



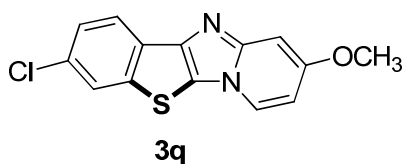
Compound **3n**: Eluent petroleum ether/ethyl acetate (5:1). 1H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.15 (d, 1H, J = 8.0 Hz), 8.09 (d, 1H, J = 8.0 Hz), 7.82 (s, 1H), 7.76 (d, 1H, J = 8.0 Hz), 7.48 (d, 1H, J = 8.0 Hz), 7.28 (t, 1H, J = 8.0 Hz), 6.92 (t, 1H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 149.7, 148.2, 145.2, 141.1, 131.0, 127.5, 126.1, 124.7, 124.2, 123.9, 122.2, 118.5, 112.3. HRMS m/z calcd. for $C_{13}H_8ClN_2S$ $[M+H]^+$: 259.0097, found: 259.0093.



Compound **3o**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.10 (d, 1H, $J = 8.0$ Hz), 7.92 (d, 1H, $J = 8.0$ Hz), 7.77 (s, 1H), 7.44 (d, 2H, $J = 8.0$ Hz), 6.71 (d, 1H, $J = 8.0$ Hz), 2.45 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 150.2, 144.9, 140.9, 135.9, 130.6, 127.6, 125.9, 123.8, 123.3, 122.1, 121.9, 116.7, 114.9, 21.6. HRMS m/z calcd. for $\text{C}_{14}\text{H}_{10}\text{ClN}_2\text{S}$ $[\text{M}+\text{H}]^+$: 273.0253, found: 273.0259.

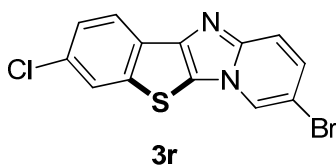


Compound **3p**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.23 (d, 1H, $J = 8.0$ Hz), 7.98 (d, 1H, $J = 8.0$ Hz), 7.82 (s, 1H), 7.48 (d, 1H, $J = 8.0$ Hz), 7.09 (d, 1H, $J = 8.0$ Hz), 6.85 (t, 1H, $J = 8.0$ Hz), 2.74 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 150.2, 144.5, 141.0, 130.8, 128.5, 127.6, 125.9, 123.8, 123.7, 123.0, 122.3, 122.0, 112.4, 17.4. HRMS m/z calcd. for $\text{C}_{14}\text{H}_{10}\text{ClN}_2\text{S}$ $[\text{M}+\text{H}]^+$: 273.0253, found: 273.0259.

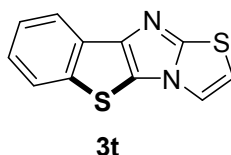


Compound **3q**: Eluent petroleum ether/ethyl acetate (3:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.07 (d, 1H, $J = 8.0$ Hz), 7.88 (d, 1H, $J = 8.0$ Hz), 7.77 (s, 1H), 7.43 (d, 1H, $J = 8.0$ Hz), 6.97 (s, 1H), 6.63 (d, 1H, $J = 4.0$ Hz), 3.90 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 158.0, 151.4, 144.7, 140.6, 130.3, 127.5, 125.9, 124.5, 123.8, 121.9, 121.4, 107.7, 95.5, 55.6. HRMS m/z calcd. for $\text{C}_{14}\text{H}_{10}\text{ClN}_2\text{OS}$ $[\text{M}+\text{H}]^+$: 289.0202,

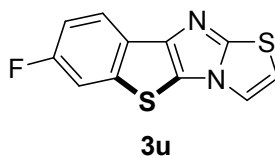
found: 289.0207.



Compound **3r**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.27 (s, 1H), 8.14 (d, 1H, $J = 8.0$ Hz), 7.83 (s, 1H), 7.66 (d, 1H, $J = 8.0$ Hz), 7.49 (d, 1H, $J = 8.0$ Hz), 7.35 (d, 1H, $J = 8.0$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 148.1, 145.8, 141.1, 131.6, 128.2, 127.1, 126.3, 124.1, 124.0, 122.7, 122.4, 118.9, 107.0. HRMS m/z calcd. for $\text{C}_{13}\text{H}_7\text{BrClN}_2\text{S}$ $[\text{M}+\text{H}]^+$: 336.9202, 338.9181, found: 336.9207, 338.9184.

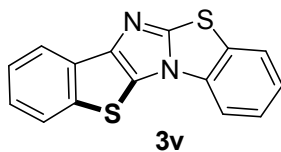


Compound **3t**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.14 (d, 1H, $J = 8.0$ Hz), 7.83 (d, 1H, $J = 8.0$ Hz), 7.57 (d, 1H, $J = 4.0$ Hz), 7.50 (t, 1H, $J = 16.0$ Hz), 7.38 (t, 1H, $J = 8.0$ Hz), 6.96 (d, 1H, $J = 4.0$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 153.5, 147.7, 138.6, 129.2, 125.3, 124.5, 124.0, 120.7, 117.2, 112.2. HRMS m/z calcd. for $\text{C}_{11}\text{H}_7\text{N}_2\text{S}$ $[\text{M}+\text{H}]^+$: 231.0051, found: 231.0050.



Compound **3u**: Eluent petroleum ether/ethyl acetate (5:1). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.07 (dd, 1H, $J = 4.0$ Hz), 7.58-7.52 (m, 2H), 7.24 (t, 1H, $J = 8.0$ Hz), 6.98 (d, 1H, $J = 4.0$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 161.4, 159.2, 153.8, 139.5 (d, $J_{\text{F-C}} = 128.2$ Hz), 126.3, 125.6, 121.4 (d, $J_{\text{F-C}} = 36.1$ Hz), 117.2, 113.7 (d, $J_{\text{F-C}} = 92.2$

Hz), 112.3, 110.5 (d, $J_{F-C} = 104.2$ Hz). HRMS m/z calcd. for $C_{11}H_6FN_2S$ $[M+H]^+$: 248.9956, found: 248.9954.



Compound **3v**: Eluent petroleum ether/ethyl acetate (5:1). 1H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.15 (d, 1H, $J = 8.0$ Hz), 7.86 (d, 1H, $J = 8$ Hz), 7.75 (d, 1H, $J = 8.0$ Hz), 7.63 (d, 1H, $J = 8.0$ Hz), 7.52 (dd, 2H, $J = 8.0$ Hz), 7.40-7.36 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 151.0, 147.0, 138.9, 131.2, 129.2, 128.8, 126.5, 125.4, 124.9, 124.3, 124.3, 124.0, 120.6, 112.6. HRMS m/z calcd. for $C_{15}H_9N_2S$ $[M+H]^+$: 281.0207, found: 281.0209.

