Supporting Information

^{1}H NMR and ^{13}C NMR Data

*N-(3-cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)-2-iodobenzamide (**BZ02**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.82-1.88 (m, 4H, 2CH_2), 2.57-2.59 (m, 4H, 2CH_2), 7.32-7.37 (td, 1H, Ar-H, *J* = 2.2, 7.6 Hz), 7.56-7.59 (m, 2H, Ar-H), 8.02 (d, 1H, Ar-H, *J* = 8 Hz), 12.35 (s, 1H, NH). ^{13}C NMR (DMSO-*d6*, δ ppm): 23.24, 24.13, 24.95, 25.11, 95.94, 115.47, 129.49, 129.67, 130.03, 131.56, 132.99, 140.36, 142.05, 142.57, 147.32, 168.56. HRMS (ESI): Calculated for $C_{16}H_{13}IN_2OS$ $(M+H)^+$, 408.9872; found, 408.9867.

*2-Bromo-N-(3-cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)benzamide (**BZ03**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.74-1.77 (m, 4H, 2CH_2), 2.48-2.62 (m, 4H, 2CH_2), 7.42-7.47 (m, 2H, Ar-H), 7.53-7.56 (m, 1H, Ar-H), 7.71-7.73 (m, 1H, Ar-H), 12.29 (s, 1H, NH). ^{13}C NMR (DMSO-*d6*, δ ppm): 23.23, 24.12, 24.94, 25.10, 95.97, 115.49, 120.76, 121.44, 129.12, 130.82, 132.09, 133.27, 134.10, 135.27, 147.22. HRMS (ESI): Calculated for $C_{16}H_{13}BrN_2OS$ $(M+H)^+$, 361.0000; found, 361.0010.

*3-Bromo-N-(3-cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)benzamide (**BZ04**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.73-1.76 (m, 4H, 2CH_2), 2.49-2.61 (m, 4H, 2CH_2), 7.50 (t, 1H, Ar-H, *J* = 7.8 Hz), 7.81-7.93 (m, 2H, Ar-H), 8.12 (s, 1H, Ar-H), 11.80 (s, 1H, NH). ^{13}C NMR (DMSO-*d6*, δ ppm): 23.22, 24.11, 24.98, 25.14, 97.66, 115.66, 123.08, 129.02, 130.35, 132.19, 132.31, 133.00, 133.25, 136.13, 136.60, 147.42, 165.24. HRMS (ESI): Calculated for $C_{16}H_{13}BrN_2OS$ $(M+H)^+$, 361.0010; found, 361.0006.

*4-Bromo-N-(3-cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)benzamide (**BZ05**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.83-1.8d (m, 4H, 2CH_2), 2.58-2.72 (m, 4H, 2CH_2), 7.87 (d, 2H, Ar-H, *J* = 16.0 Hz), 7.98 (d, 2H, Ar-H, *J* = 8.0 Hz), 11.87 (s, 1H, NH). HRMS (ESI): Calculated for $C_{16}H_{13}BrN_2OS$ $(M+H)^+$, 361.0010; found, 361.0012.

*2-((2-Iodobenzyl)amino)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile (**BZA06**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.60-1.74 (s, 4H, 2CH_2), 2.35-2.39 (m, 4H, 2CH_2), 4.28 (d, 2H, CH_2, *J* = 5.6 Hz), 7.04 (td, 1H, Ar-H, *J* = 1.6, 7.8 Hz), 7.30 (d, 1H, Ar-H, *J*= 7.6 Hz), 7.38 (td, 1H, Ar-H, *J* = 1.0, 7.6Hz), 7.85 (d, 1H, Ar-H, *J* = 7.6 Hz), 8.09 (t, 1H, NH, *J* = 5.6 Hz). ^{13}C NMR (DMSO-*d6*, δ ppm): 23.24, 24.38, 25.01, 25.53, 56.60, 83.96, 100.38, 117.69, 119.02, 129.46, 129.98, 130.89, 133.72, 140.68, 140.76, 164.17. HRMS (ESI): Calculated for $C_{16}H_{15}IN_2S$ $(M+H)^+$, 395.0079; found, 395.0077.

*2-((2-Bromobenzyl)amino)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile (**BZA07**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.65-1.68 (m, 4H, 2CH_2), 2.35-2.39 (m, 4H, 2CH_2), 4.37 (d, 2H, CH_2, *J* = 6.0 Hz), 7.20-7.24 (m, 1H, Ar-H), 7.34-7.40 (m, 2H, Ar-H), 7.61 (d, 1H, Ar-H, *J* = 8.0 Hz), 8.09 (t, 1H, NH, *J* = 6.0 Hz). ^{13}C NMR (DMSO-*d6*, δ ppm): 23.23, 24.36, 24.99, 25.51, 51.65, 83.98, 117.64, 118.98, 124.10, 129.42, 130.05, 130.84, 133.74, 134.13, 138.06, 164.23. HRMS (ESI): Calculated for $C_{16}H_{15}BrN_2S$ $(M+H)^+$, 347.0218; found, 347.0209.

*2-((3-Bromobenzyl)amino)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile (**BZA08**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.74-1.76 (m, 4H, $2CH_2$), 2.43-2.47 (m, 4H, $2CH_2$), 4.42 (d, 2H, CH_2, *J* = 6.0 Hz), 7.36-7.43 (m, 1H, Ar-H), 7.53 (d, 2H, Ar-H, *J* = 7.6 Hz), 7.62 (s, 1H, Ar-H), 8.17 (t, 1H, NH, *J* = 6.0 Hz). ^{13}C NMR (DMSO-*d6*, δ ppm): 23.23, 24.38, 25.00, 25.49, 50.74, 83.91, 117.77, 118.97, 123.26, 127.90, 131.39, 131.58, 132.15, 133.61, 142.79, 164.34. HRMS (ESI): Calculated for $C_{16}H_{15}BrN_2S$ $(M_+H)^+$, 347.0218; found, 347.0212.

*2-((4-Bromobenzyl)amino)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile (**BZA09**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.63-1.71 (m, 4H, $2CH_2$), 2.33-2.38 (m, 4H, $2CH_2$), 4.30 (d, 2H, CH_2, *J* = 5.6 Hz), 7.28 (d, 2H, Ar-H, *J* = 8.4 Hz), 7.53 (d, 2H, Ar-H, *J* = 10.8 Hz), 8.08 (t, 1H, NH, *J* = 6.6 Hz). ^{13}C NMR (DMSO-*d6*, δ ppm): 23.19, 24.38, 24.99, 25.48, 50.69, 83.84, 117.75, 118.87, 121.74, 130.99, 132.83, 133.53, 139.28, 164.35. HRMS (ESI): Calculated for $C_{16}H_{15}BrN_2S$ $(M_+H)^+$, 347.0218; found, 347.0203.

2-((2-Fluorobenzyl)amino)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile (***BZA10***)

^{1}H NMR (DMSO-*d6*, δ ppm): 1.67-1.68 (m, 4H, $2CH_2$), 2.34-2.39 (m, 4H, $2CH_2$), 4.38 (d, 2H, CH_2, *J* = 5.6 Hz), 7.18 (t, 2H, Ar-H, *J* = 8.4 Hz), 7.29-7.32 (m, 1H, Ar-H), 7.35-7.39 (m, 1H, Ar-H), 8.02 (t, 1H, NH, *J* = 6.0 Hz). ^{13}C NMR (DMSO-*d6*, δ ppm): 23.23, 24.37, 24.99, 25.49, 45.08, 83.91, 116.66, 116.87, 117.70, 118.88, 125.97,126.00, 130.75, 130.89, 133.65, 164.23. HRMS (ESI): Calculated for $C_{16}H_{15}FN_2S$ $(M_+H)^+$, 287.1018; found, 287.1007.

*2-((Naphthalen-1-ylmethyl)amino)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile (**BZA11**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.78-1.86 (m, 4H, $2CH_2$), 2.51-2.55 (m, 4H, $2CH_2$), 4.81 (s, 2H, CH_2), 7.26 (m, 4H, Ar-H), 7.85-7.98 (m, 3H, Ar-H). HRMS (ESI): Calculated for $C_{20}H_{18}N_2S$ $(M_+H)^+$, 319.1269; found, 319.1260.

*1-(3-Cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)-3-phenylurea (**BU12**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.81-1.87 (m, 4H, $2CH_2$), 2.58-2.61 (m, 4H, $2CH_2$), 7.11 (t, 1H, Ar-H, *J* = 6.0 Hz), 7.34 (t, 2H, Ar-H, *J* = 7.6 Hz), 7.46 (d, 2H, Ar-H, *J* = 8.0 Hz), 7.65 (s, 1H, NH).

*1-(2-Bromophenyl)-3-(3-cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)urea (**BU13**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.74 (m, 4H, $2CH_2$), 2.47-2.50 (m, 4H, $2CH_2$), 7.02 (t, 1H, Ar-H, *J* = 8.0 Hz), 7.35 (t, 1H, Ar-H, *J* = 8.0 Hz), 7.63 (d, 1H, Ar-H, *J* = 8.0 Hz), 8.00 (d, 1H, Ar-H, *J* = 8.0 Hz), 8.84 (s, 1H, NH), 10.84 (s, 1H, NH). ^{13}C NMR (DMSO-*d6*, δ ppm): 23.24, 24.17, 24.80, 25.00, 91.64, 114.89, 116.21, 124.08, 126.47, 127.47, 129.64, 131.69, 134.13, 137.65, 150.43, 152.48. HRMS (ESI): Calculated for $C_{16}H_{14}BrN_3OS$ $(M_+H)^+$, 376.0123; found, 376.0119.

*1-(3-Cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)-3-(p-tolyl)urea (**BU14**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.68-1.78 (m, 4H, $2CH_2$), 2.24 (s, 3H, CH_3), 2.49-2.55 (m, 4H, $2CH_2$), 7.11 (d, 2H, Ar-H, *J* = 7.6 Hz), 7.31 (d, 2H, Ar-H, *J* = 8.0 Hz), 9.09 (s, 1H, NH), 10.04 (s, 1H, NH). HRMS (ESI): Calculated for $C_{17}H_{17}N_3OS$ $(M_+H)^+$, 312.1160; found, 312.1130.

*1-(3-Cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)-3-(4-methoxyphenyl)urea (**BU15**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.65-1.87 (m, 4H, $2CH_2$), 2.51-2.58 (m, 4H, $2CH_2$), 3.80 (s, 3H, CH_3), 6.88 (d, 2H, Ar-H, *J* = 8.0 Hz), 7.35 (d, 2H, Ar-H, *J* = 7.6 Hz), 7.52 (s, 1H, NH), 8.63 (s, 1H, NH). ^{13}C NMR (DMSO-*d6*, δ ppm): 23.22, 24.20, 24.80, 24.99, 56.66, 91.00, 115.46, 116.36, 121.50, 126.82, 131.40, 132.82, 151.10, 152.30, 156.40. HRMS (ESI): Calculated for $C_{17}H_{17}N_3O_2S$ $(M_+H)^+$, 328.1118; found, 328.1120.

*1-(4-Butylphenyl)-3-(3-cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)urea (**BU16**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 0.93 (t, 3H, CH_3, *J* = 6.0 Hz), 1.30-1.39 (m, 2H, CH_2), 1.54-1.61 (m, 2H, CH_2), 1.80 (m, 4H, $2CH_2$), 2.50 (t, 2H, CH_2, *J* = 6.0 Hz), 2.55-2.59 (m, 4H, $2CH_2$), 7.13 (d, 2H, Ar-H, *J* = 8.0 Hz), 7.33 (d, 2H, Ar-H, *J* = 8.0 Hz), 7.69 (s, 1H, NH), 8.78 (s, 1H, NH). ^{13}C NMR (DMSO-*d6*, δ ppm): 15.00, 23.17, 23.35, 24.41, 24.95, 34.73, 36.07, 117.26, 120.81, 121.64, 127.83, 130.06, 131.21, 133.31, 136.31, 139.69, 152.21. HRMS (ESI): Calculated for $C_{20}H_{23}N_3OS$ $(M_+H)^+$, 354.1632; found, 354.1640.

*1-Benzyl-3-(3-cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)urea (**BU17**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.79-1.85 (m, 4H, $2CH_2$), 2.40-2.56 (m, 4H, $2CH_2$), 4.46 (d, 2H, CH_2, *J* = 8.0 Hz), 6.11 (s, 1H, NH), 7.25-7.31 (m, 5H, Ar-H), 8.75 (s, 1H, NH). ^{13}C NMR (DMSO-*d6*, δ ppm): 23.21, 24.21, 24.90, 24.95, 45.32, 90.12, 117.17, 127.22, 128.44 128.50, 129.70, 131.14, 139.30, 152.76, 154.78. HRMS (ESI): Calculated for $C_{17}H_{17}N_3OS$ $(M_+H)^+$, 312.1163; found, 312.1171.

*1-(3-cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)-3-(4-methoxybenzyl)urea (**BU18**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.69- 1.74 (m, 4H, $2CH_2$), 2.44-2.50 (m, 4H, $2CH_2$), 3.73 (s, 3H, OCH_3), 4.25 (d, 2H, CH_2, *J* = 8.0 Hz), 6.89-6.92 (d, 2H, Ar-H, *J* = 12.0 Hz), 7.14 (t, 1H, NH, *J* = 8.0 Hz), 7.23(d, 2H, Ar-H, *J* = 12.0 Hz), 9.96 (s, 1H, NH). HRMS (ESI): Calculated for $C_{18}H_{19}N_3O_2S$ $(M_+H)^+$, 342.1269; found, 342.1276.

*1-(4-Chloro-3-(trifluoromethyl)phenyl)-3-(3-cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)urea (**BU19**)*

^{1}H NMR (DMSO-*d6*, δ ppm): 1.69- 1.74 (m, 4H, $2CH_2$), 2.44-2.50 (m, 4H, $2CH_2$), 7.56-7.60 (m, 2H, Ar-H), 8.12 (s, 1H, Ar-H), 9.55 (s, 1H, NH), 10.42 (s, 1H, NH). HRMS (ESI): Calculated for $C_{17}H_{13}ClF_3N_3OS$ $(M_+H)^+$, 400.0501; found, 400.0498.