Reaction of 1-Acetonaphthones with Anilines and Elemental Sulfur: Rapid Construction of 1-Anilinonaphtho[2,1-*b*]thiophenes

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Supporting Information

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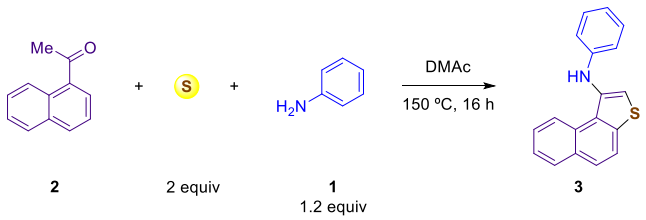
General Information

Reagents (sulfur, solvents, anilines, 1-acetonaphthones as well as other derivatives) were obtained from commercial supplier and used without further purification. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or KMnO4 or vanilline stains. Flash column chromatography was carried out using kieselgel 35-70 µm particle sized silica gel (230-400 mesh). NMR Chemical shifts are reported in (δ) ppm relative to tetramethylsilane (TMS) with the residual solvent as internal reference ($CDCl_3$, δ 7.26 ppm for ^1H and δ 77.0 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration.

General protocol for the synthesis of *N*-phenylnaphtho[2,1-*b*]thiophen-1-amines 3



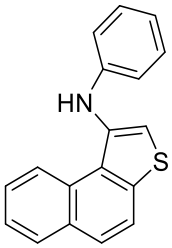
A mixture of aniline **1** (1.2 mmol), 1-acetylnaphthalene **2** (1.0 mmol), sulfur (2 mmol, 64 mg), and DMAc (0.2 mL) in a 7-mL test tube closed with a rubber septum was heated at 150 °C for 16 h. The reaction cooled to room temperature was purified by column chromatography on silica (Eluent: hexane/ethyl acetate: 95/05).

Protocol for the oxidation of 3ab into 3ab-O_2

To a stirred solution of **3ab** (0.5 mmol, 145 mg) in chloroform (1.5 mL) in a 10-mL round-bottomed flask was added in small portions of *m*-CPBA (85%, 304 mg, 1.5 mmol). The resulting solution was stirred at rt for 4 h (the reaction was followed by TLC), then quenched with an aqueous solution of sodium sulfite (20%, 2 mL). The organic layer was separated, dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography on silica gel (eluent hexane: EtOAc 9:1) to provide **3ab-O_2** as a white solid (56 mg, 36%).

Characterization data of *N*-phenylnaphtho[2,1-b]thiophen-1-amines 3

***N*-Phenylnaphtho[2,1-b]thiophen-1-amine (3aa)**



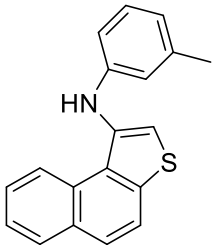
Brown solid (181 mg, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.9 (d, *J* = 7.9 Hz, 1H), 7.9 (d, *J* = 7.7 Hz, 1H), 7.8 (d, *J* = 8.8 Hz, 1H), 7.8 (d, *J* = 8.7 Hz, 1H), 7.5 – 7.4 (m, 2H), 7.3 (s, 1H), 7.2 – 7.2 (m, 2H), 6.9 – 6.8 (m, 1H), 6.8 – 6.8 (m, 2H), 5.7 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 138.4, 137.9, 131.9, 130.2, 129.7, 129.6 (2C), 128.6, 126.5, 126.1, 125.4, 123.5, 121.4, 119.7, 117.7, 115.4 (2C).

HRMS *m/z*: calcd for $[M+H]^+$ $C_{18}H_{14}NS$: 276.0847. Found: 276.0852.

***N*-(m-Tolyl)naphtho[2,1-b]thiophen-1-amine (3ab)**



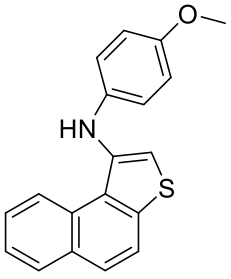
Brown solid (205 mg, 71%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.97 – 7.88 (m, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.31 (s, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 2H), 6.65 – 6.59 (m, 1H), 5.68 (s, 1H), 2.27 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 139.5, 138.6, 137.8, 131.9, 130.2, 129.8, 129.4, 128.6, 126.5, 126.1, 125.4, 123.5, 121.4, 120.7, 117.5, 116.1, 112.6, 21.7.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{19}H_{16}NS$: 290.1003. Found: 290.1007.

***N*-(4-Methoxyphenyl)naphtho[2,1-b]thiophen-1-amine (3ac)**



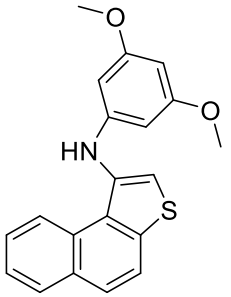
Brown solid (158 mg, 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, *J* = 9.6 Hz, 1H), 7.98 – 7.91 (m, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.13 (s, 1H), 6.86 – 6.78 (m, 4H), 5.63 (s, 1H), 3.76 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.1, 140.5, 139.9, 138.0, 131.9, 129.8, 129.6, 128.7, 126.4, 126.0, 125.3, 123.5, 121.5, 118.0 (2C), 115.1 (2C), 114.3, 55.8.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{19}H_{16}NOS$: 306.0953. Found: 306.0958.

***N*-(3,5-Dimethoxyphenyl)naphtho[2,1-b]thiophen-1-amine (3ad)**



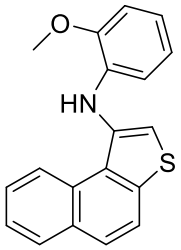
Brown solid (161mg, 48%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.93 (dd, *J* = 7.3, 1.3 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.59 – 7.51 (m, 2H), 7.31 (d, *J* = 2.1 Hz, 1H), 7.26 (s, 2H), 6.57 (d, *J* = 2.1 Hz, 1H), 4.00 (s, 3H), 3.94 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 160.6, 156.1, 154.6, 134.3, 131.2, 129.9, 129.4, 128.6, 127.8, 127.5, 126.7, 126.2, 125.3, 98.1, 97.8, 97.2, 97.0, 56.3, 56.1.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{20}H_{18}NO_2S$: 336.1058. Found: 336.1063

***N*-(2-Methoxyphenyl)naphtho[2,1-b]thiophen-1-amine (3ae)**



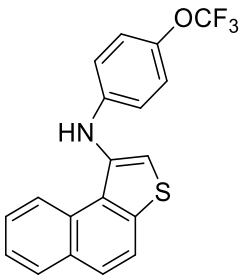
Brown solid (168 mg, 55%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.94 (dd, *J* = 7.2, 2.5 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.33 (s, 1H), 6.95 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.80 (td, *J* = 7.7, 1.7 Hz, 1H), 6.74 (td, *J* = 7.7, 1.5 Hz, 1H), 6.69 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.38 (s, 1H), 4.01 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 138.5, 137.9, 136.3, 132.0, 130.5, 129.9, 128.7, 126.6, 126.1, 125.5, 123.5, 121.6, 121.5, 119.0, 117.0, 114.0, 110.4, 56.0.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{19}H_{16}NOS$: 306.0953. Found: 306.0958

***N*-(4-(Trifluoromethoxy)phenyl)naphtho[2,1-b]thiophen-1-amine (3af)**



Brown solid (223 mg, 62%).

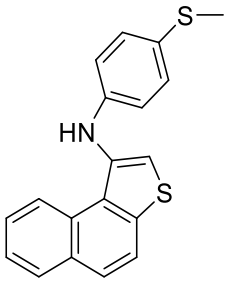
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.50 – 7.46 (m, 1H), 7.30 (s, 1H), 7.05 (d, *J* = 8.9 Hz, 2H), 6.73 (d, *J* = 8.9 Hz, 2H), 5.73 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 142.1, 142.0, 138.0, 137.7, 131.9, 130.0, 129.5, 128.7, 126.6, 126.2, 125.6, 123.2, 122.6 (2C), 121.4, 118.8, 115.6 (2C).

^{19}F NMR (471 MHz, $CDCl_3$) δ -58.30.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{19}H_{13}F_3NOS$: 360.0670. Found: 360.0677.

***N*-(4-(Methylthio)phenyl)naphtho[2,1-b]thiophen-1-amine (3ag)**



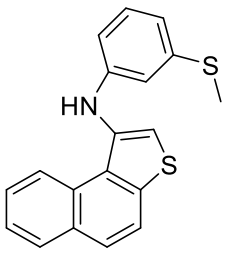
Brown solid (250 mg, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.94 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.43 (m, 2H), 7.30 (s, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 5.75 (s, 1H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 138.1, 137.9, 131.9, 130.7 (2C), 130.1, 129.6, 128.7, 127.3, 126.6, 126.2, 125.5, 123.4, 121.4, 118.0, 116.0 (2C), 18.4.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{19}H_{16}NS_2$: 322.0724. Found: 322.0727.

***N*-(3-(Methylthio)phenyl)naphtho[2,1-b]thiophen-1-amine (3ah)**



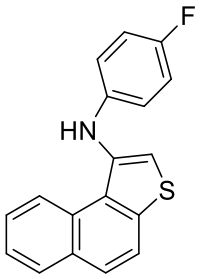
Brown solid (234 mg, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.94 (dd, *J* = 7.4, 2.2 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.32 (s, 1H), 7.10 (t, *J* = 8.2 Hz, 1H), 6.73 (dd, *J* = 6.6, 1.3 Hz, 2H), 6.57 – 6.51 (m, 1H), 5.73 (s, 1H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8, 139.5, 137.6, 137.5, 131.6, 129.9, 129.7, 129.4, 128.4, 126.3, 125.9, 125.2, 123.1, 121.2, 118.1, 117.4, 112.9, 111.9, 15.5.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{19}H_{16}NS_2$: 322.0724. Found: 322.0729.

_N_-(4-Fluorophenyl)naphtho[2,1-b]thiophen-1-amine (3ai)



Brown solid (190 mg, 65%).

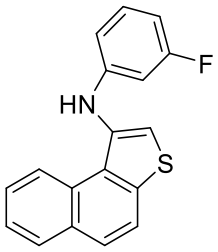
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (d, *J* = 8.1 Hz, 1H), 7.95 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.22 (s, 1H), 6.91 (t, *J* = 8.7 Hz, 2H), 6.74 (dd, *J* = 9.0, 4.4 Hz, 2H), 5.67 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2 (d, *J* = 237.5 Hz), 142.6 (d, *J* = 2.3 Hz), 139.0, 138.0, 131.9, 129.8, 129.6, 128.7, 126.5, 126.1, 125.5, 123.4, 121.5, 116.9, 116.8 (d, *J* = 7.6 Hz) (2C), 116.1 (d, *J* = 22.4 Hz) (2C).

^{19}F NMR (471 MHz, $CDCl_3$) δ -124.93.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{18}H_{13}FNS$: 294.0753. Found: 294.0756

_N_-(3-Fluorophenyl)naphtho[2,1-b]thiophen-1-amine (3aj)



Brown solid (214 mg, 73%).

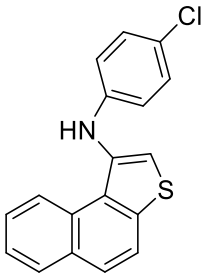
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.2 Hz, 1H), 7.96 – 7.92 (m, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.50 – 7.46 (m, 1H), 7.35 (s, 1H), 7.13 (td, *J* = 8.1, 6.5 Hz, 1H), 6.57 – 6.48 (m, 2H), 6.45 (dt, *J* = 11.2, 2.3 Hz, 1H), 5.77 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2 (d, *J* = 244.0 Hz), 148.5 (d, *J* = 10.5 Hz), 138.0, 137.0, 131.9, 130.7 (d, *J* = 10.0 Hz), 130.1, 129.5, 128.7, 126.6, 126.2, 125.5, 123.2, 121.4, 119.6, 110.6 (d, *J* = 3.4 Hz), 106.0 (d, *J* = 21.5 Hz), 101.9 (d, *J* = 25.7 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -112.24.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{18}H_{13}FNS$: 294.0753. Found: 294.0758.

_N_-(4-Chlorophenyl)naphtho[2,1-b]thiophen-1-amine (3ak)



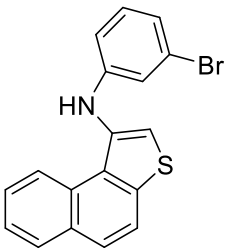
Brown solid (139 mg, 45%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.49 – 7.44 (m, 1H), 7.31 (s, 1H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 5.74 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 138.0, 137.7, 131.9, 130.0, 129.5, 129.4 (2C), 128.7, 126.6, 126.3, 125.5, 124.3, 123.3, 121.4, 118.6, 116.3 (2C).

HRMS *m/z*: calcd for $[M+H]^+$ $C_{18}H_{13}ClNS$: 310.0457. Found: 310.0459.

N-(3-bromophenyl)naphtho[2,1-b]thiophen-1-amine (3al)



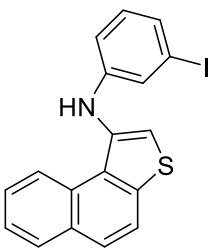
Brown solid (232 mg, 66%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.93 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.34 (s, 1H), 7.01 (t, *J* = 8.3 Hz, 1H), 6.97 – 6.89 (m, 2H), 6.67 – 6.61 (m, 1H), 5.71 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 137.9, 136.8, 131.8, 130.8, 130.0, 129.4, 128.6, 126.6, 126.2, 125.5, 123.3, 123.0, 122.2, 121.3, 119.5, 117.6, 113.4.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{18}H_{13}BrNS$: 353.9952. Found: 353.9958

N-(3-iodophenyl)naphtho[2,1-b]thiophen-1-amine (3am)



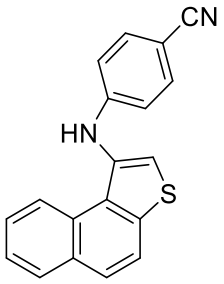
Brown solid (192 mg, 48%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.95 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.50 (pd, *J* = 7.0, 1.6 Hz, 2H), 7.34 (s, 1H), 7.18 (t, *J* = 2.0 Hz, 1H), 7.15 (dt, *J* = 7.7, 1.2 Hz, 1H), 6.87 (t, *J* = 7.9 Hz, 1H), 6.68 (dd, *J* = 8.1, 1.6 Hz, 1H), 5.67 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 137.8, 136.9, 131.8, 130.9, 129.9, 129.4, 128.6, 128.3, 126.6, 126.2, 125.5, 123.5, 123.0, 121.3, 119.3, 114.0, 95.2.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{18}H_{13}INS$: 401.9813. Found: 401.9816.

4-(Naphtho[2,1-b]thiophen-1-ylamino)benzonitrile (3an)



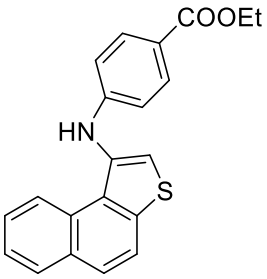
Brown solid (141 mg, 47%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.48 – 7.42 (m, 4H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.12 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 138.2, 135.0, 134.1 (2C), 131.9, 130.0, 129.2, 128.9, 126.8, 126.6, 125.8, 122.8, 121.8, 121.4, 120.1, 114.2 (2C), 101.3.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{19}H_{13}N_2S$: 301.0799. Found: 301.0792.

Ethyl 4-(naphtho[2,1-b]thiophen-1-ylamino)benzoate (3ao)



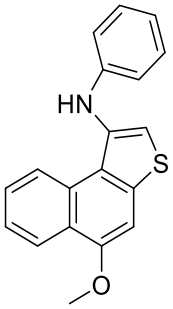
Brown solid (146 mg, 42%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.94 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.49 (ddd, *J* = 8.0, 6.9, 1.3 Hz, 1H), 7.43 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.41 (s, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.06 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 150.6, 137.9, 135.9, 131.7, 131.6, 130.0, 129.3, 128.6, 126.6, 126.2, 125.5, 123.0, 121.3, 120.9, 120.7, 113.5, 60.4, 14.4.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{21}H_{18}NO_2S$: 348.1058. Found: 348.1062.

5-Methoxy-*N*-phenylnaphtho[2,1-b]thiophen-1-amine (3ba)



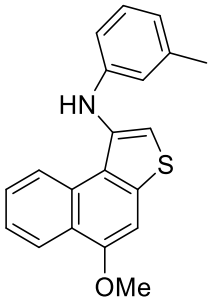
Brown solid (146 mg, 48%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 7.9 Hz, 1H), 8.36 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.20 – 7.19 (m, 2H), 7.10 (s, 1H), 6.84 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.82 – 6.79 (m, 2H), 5.70 (s, 1H), 4.07 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 146.6, 138.6, 138.1, 130.1, 129.5 (2C), 127.1, 125.1, 125.0, 124.3, 123.2, 122.7, 119.6, 115.4 (2C), 114.3, 99.2, 55.9.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{19}H_{16}NOS$: 306.0953. Found: 306.0958.

5-Methoxy-*N*-(m-tolyl)naphtho[2,1-b]thiophen-1-amine (3bb)



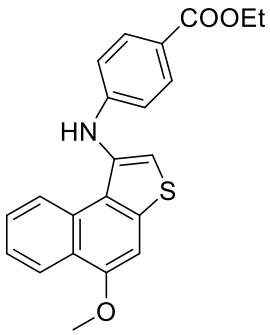
Brown solid (137 mg, 43%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 8.1, 1.8 Hz, 1H), 8.37 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.19 (s, 1H), 7.11 – 7.07 (m, 2H), 6.70 – 6.63 (m, 2H), 6.62 (dd, *J* = 7.9, 2.3 Hz, 1H), 5.62 (s, 1H), 4.07 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 146.6, 139.4, 138.5, 138.2, 130.1, 129.4, 127.1, 125.1, 125.0, 124.3, 123.2, 122.7, 120.5, 116.1, 114.2, 112.5, 99.2, 55.8, 21.7.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{20}H_{18}NOS$, 320.1109. Found: 320.1113.

Ethyl 4-((5-methoxynaphtho[2,1-b]thiophen-1-yl)amino)benzoate (3bo)



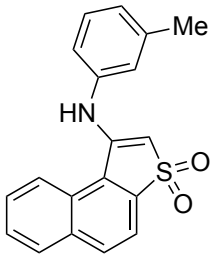
Brown solid (124 mg, 33%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 – 8.58 (m, 1H), 8.36 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.94 – 7.79 (m, 2H), 7.49 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.44 (ddd, *J* = 8.4, 6.9, 1.6 Hz, 1H), 7.20 (d, *J* = 3.6 Hz, 2H), 6.75 – 6.66 (m, 2H), 6.03 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.08 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 154.0, 150.7, 138.7, 135.6, 131.6, 129.6, 127.2, 125.1, 125.0, 124.0, 122.7, 120.8, 117.2, 113.5, 99.0, 60.4, 14.4.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{22}H_{20}NO_3S$, 378.1164. Found: 378.1169.

1-(*m*-Tolylamino)naphtho[2,1-*b*]thiophene 3,3-dioxide (3ab-O_2)



^{1}H NMR (500 MHz, DMSO-d_6) δ 9.16 (dq, *J* = 8.5, 0.9 Hz, 1H), 8.71 (d, *J* = 9.2 Hz, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 7.96 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.91 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 9.4 Hz, 1H), 7.41 (s, 1H), 7.40 (dd, *J* = 7.7, 1.1 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, DMSO) δ 159.0, 139.6, 137.5, 136.5, 135.6, 130.9, 130.8, 129.8, 129.7, 129.5, 129.4, 128.5, 127.7, 126.2, 125.0, 121.3, 115.9, 20.7.

HRMS *m/z*: calcd for $[M+H]^+$ $C_{19}H_{16}NO_2S$: 322.0902. Found: 322.0917.

Crystallographic data collection, structure determination and refinement for 3aa

Suitable crystals for single crystal X-ray diffraction (SCXRD) analysis were obtained for the molecule of interest by slow evaporation of a solution of the compound **3aa** in $CDCl_3$ in an NMR tube

X-ray diffraction data were measured at room temperature using a RIGAKU *XtaLabPro* diffractometer equipped with a Mo microfocus sealed tube *MM003* generator coupled to a double-bounce confocal Max-Flux® multilayer optic and a HPAD *PILATUS3R 200K* detector. *CrysAlisPro 1.171.42.64a*[1] was employed for the data processing, with absorption correction based upon an empirical one using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Its original structure was readily solved by intrinsic phasing methods (*SHELXT* program),[2] and all were refined by full-matrix least-squares methods on F^2 using *SHELX-L*.[3] Structural parameters for all non-hydrogen atoms of **3aa** were improved by anisotropic refinement. Furthermore, if most of the H atoms could be identified in difference maps, the aromatic H atoms were positioned geometrically and refined with U_{iso} set to $1.2U_{eq}$(C) of the parent carbon atom whereas the amine H atom was freely refined. All atoms from the naphto-thiophen platform were subject to rigid bond restraints as well as anisotropic displacement parameter ones (*DELU* -with sigma for 1-2 distances of 0.005 and sigma for 1-3 distances of 0.005- and *SIMU* -within 2A with sigma of 0.01 and sigma for terminal atoms of 0.01 within 2Å- instructions) to make the ellipsoids similar throughout it. One molecule of interest occupies the asymmetric unit of the orthorhombic P 2_1 2_1 2_1 (space group n°19) unit cell. The phenyl plane is almost orthogonal to the naptho-thiophen platform (dihedral angle of 86.6°) with its direction about 45° out of the platform mean plane bridged by the amine group. The amine hydrogen atom is making a N-H… c_g (π-ring) interaction with the naphtalen moiety of the vicinal molecule at x+1, y, z, with the following parameters d (H… c_g) = 2.67(6)Å, ∠ (H… c_g) = 155(6)°, d (N… c_g) = 3.442(4)Å. A search of the Cambridge Structural Database (CSD Version 5.43, November 2021 update Sep 2022[4]) revealed no hits of phenyl thiophen moiety substituted by a nitrogen at the C1 position of the thiophen group.

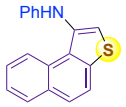
Crystal data, data collection and structure refinement details are summarized in Table S1.

CCDC 2212955 (compound **3aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

1 Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, Oxfordshire, England.
2 Sheldrick, G. M. (2015). *Acta Crystallogr.,* **C**71, 3-8.
3 Sheldrick, G. M. (2015). *Acta Crystallogr.,* **A**71, 3-8.
4 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Table S1 Crystal data, data collection and structure refinement details for **3aa**

Compound	**3aa**
2D-scheme	
Chemical name	*N*-phenylnaphtho[2,1-*b*]thiophen-1-amine
Empirical formula	$C_{18}H_{13}NS$
Formula weight	275.35
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, P $2_12_12_1$
Unit cell dimensions | (Å)	5.7573(3) 8.3305(6) 30.537(2)
Volume ($Å^3$)	1464.58(16)
Z, Calculated density (Mg/m^3)	4, 1.249
Absorption coefficient (mm^{-1})	0.209
F(000)	576
Crystal size (mm)	0.22 x 0.16 x 0.04
θ range for data collection (°)	2.534 to 25.347
Limiting indices	$-5 \le h \le 6$, $-10 \le k \le 10$, $-36 \le l \le 36$
Reflections collected / unique [R(int)	14049 / 2666 0.0420
Completeness to θ_{full} = 25.3 (%)	99.8
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.88192 and 0.16952
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters		2665 / 126 / 185
Goodness-of-fit on F^2		1.027
Final R indices [$I>2\sigma(I)$]	R1, wR2	0.0434, 0.1075
R indices (all data)	R1, wR2	0.0588, 0.1166
Absolute structure parameter		0.05 (5)
Largest Δ peak and hole (e.Å^{-3})		0.135 and -0.221
CCDC deposit number		2212955

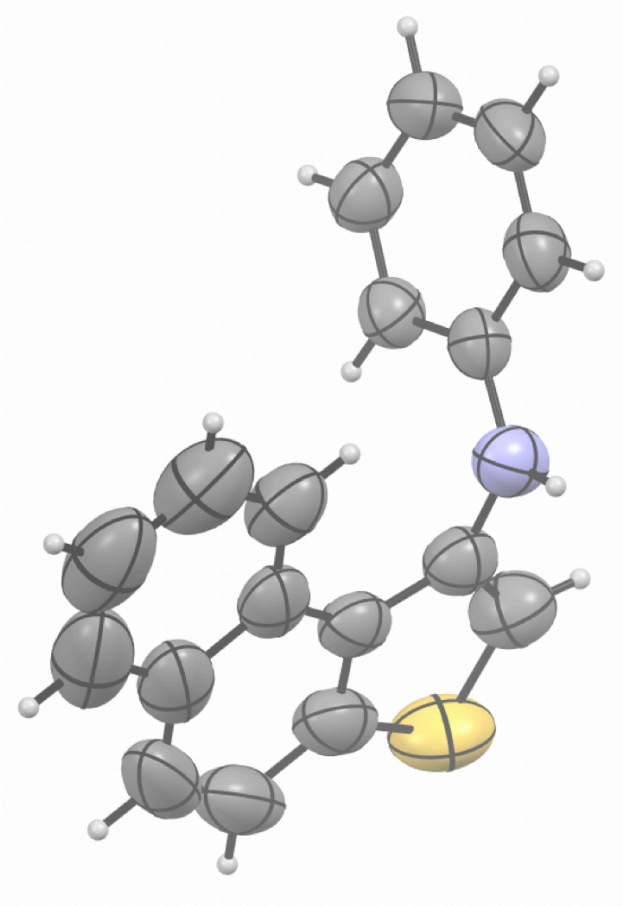
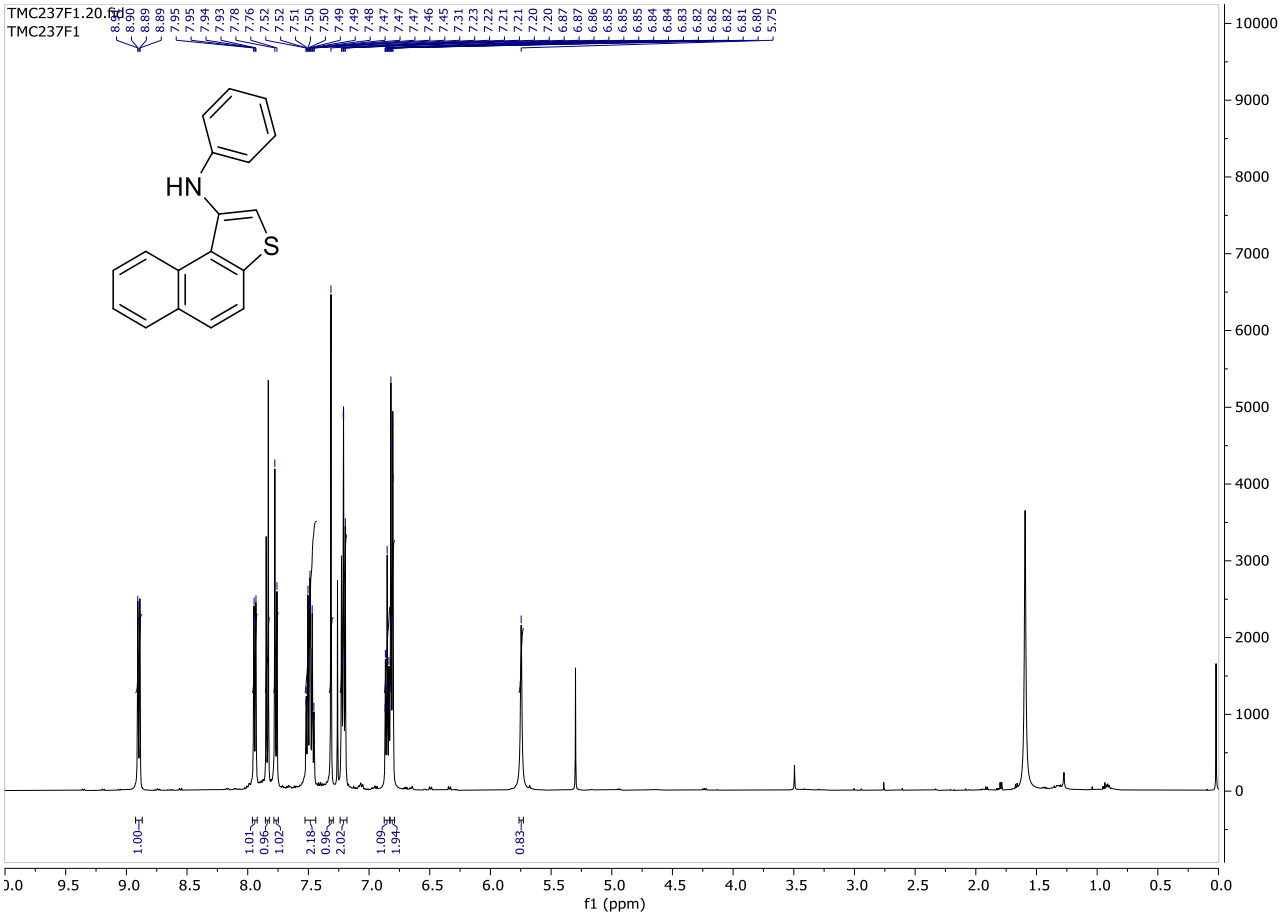
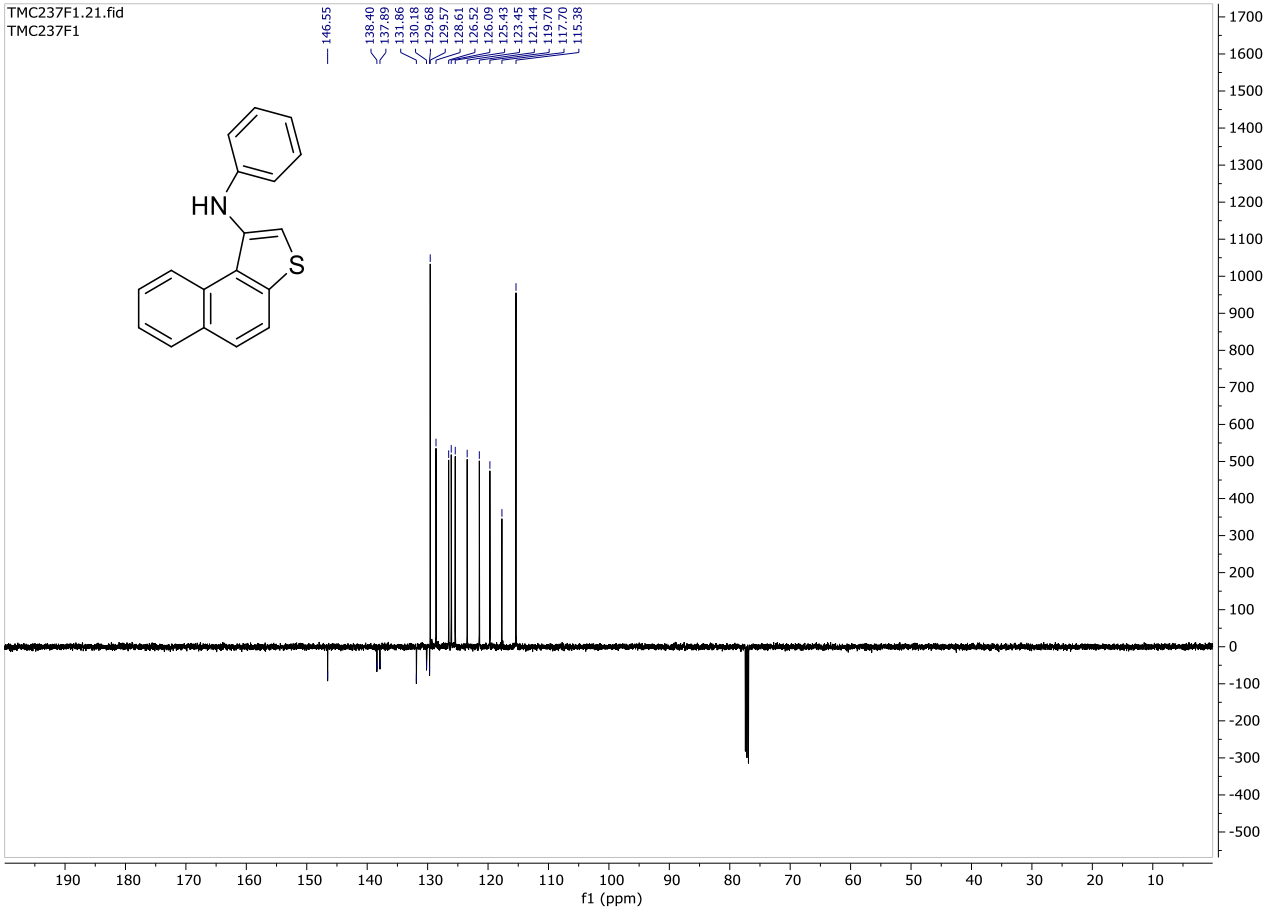


Figure 1 Ortep view of **3aa**. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms with an arbitrary radius size.

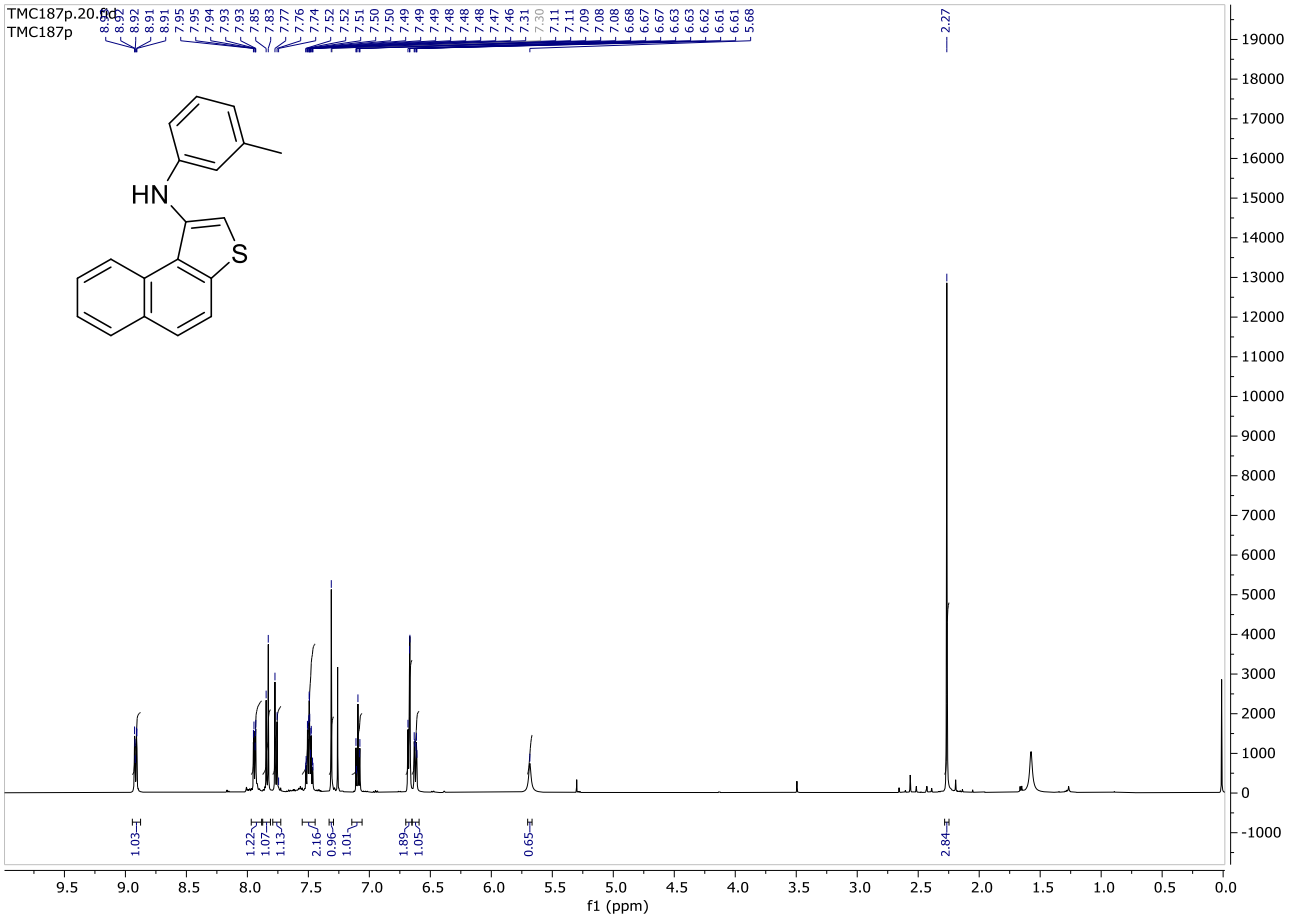
Copies of ^{1}H and ^{13}C spectra of *N*-phenylnaphtho[2,1-b]thiophen-1-amines

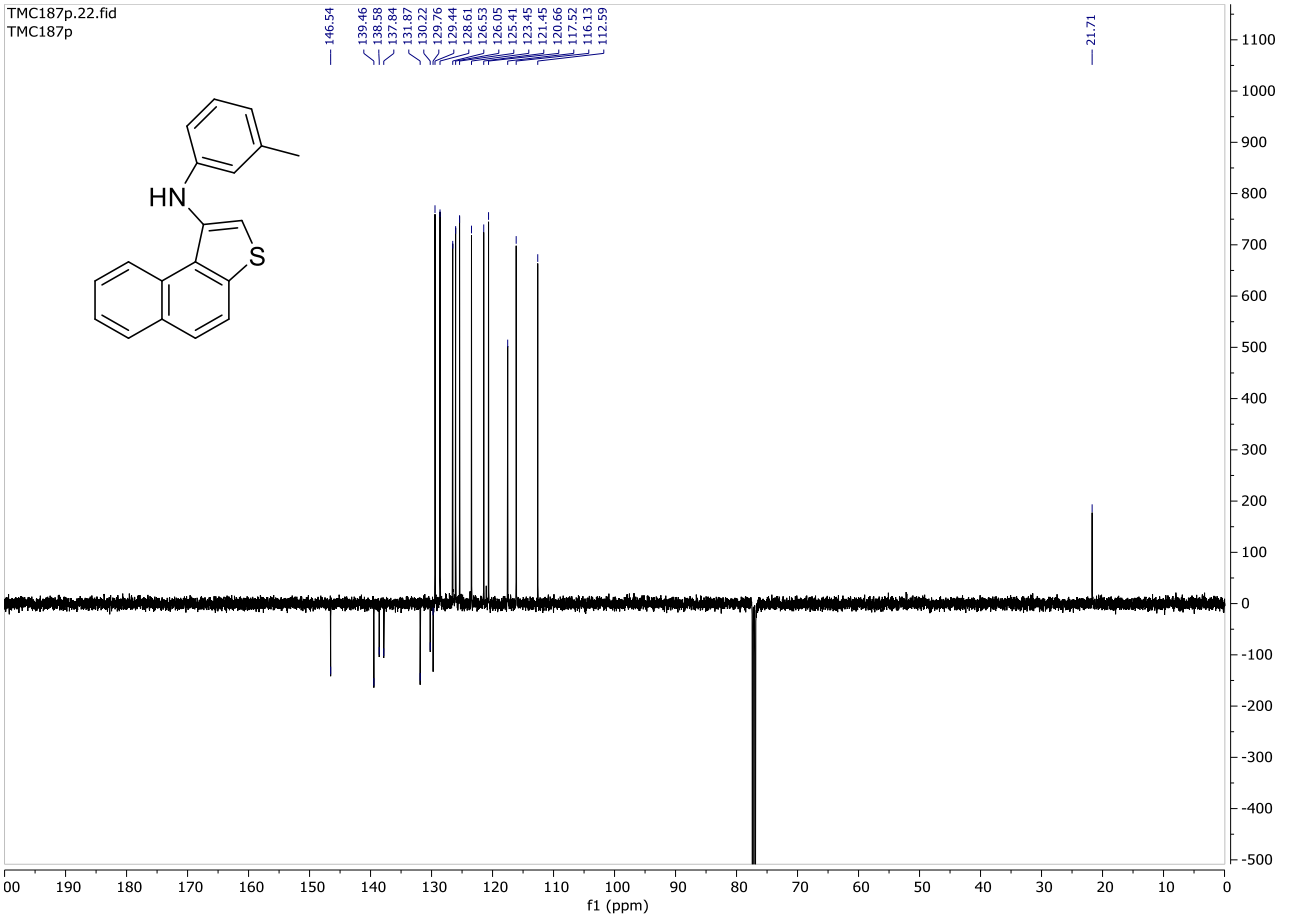
N-Phenylnaphtho[2,1-b]thiophen-1-amine (3aa) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)



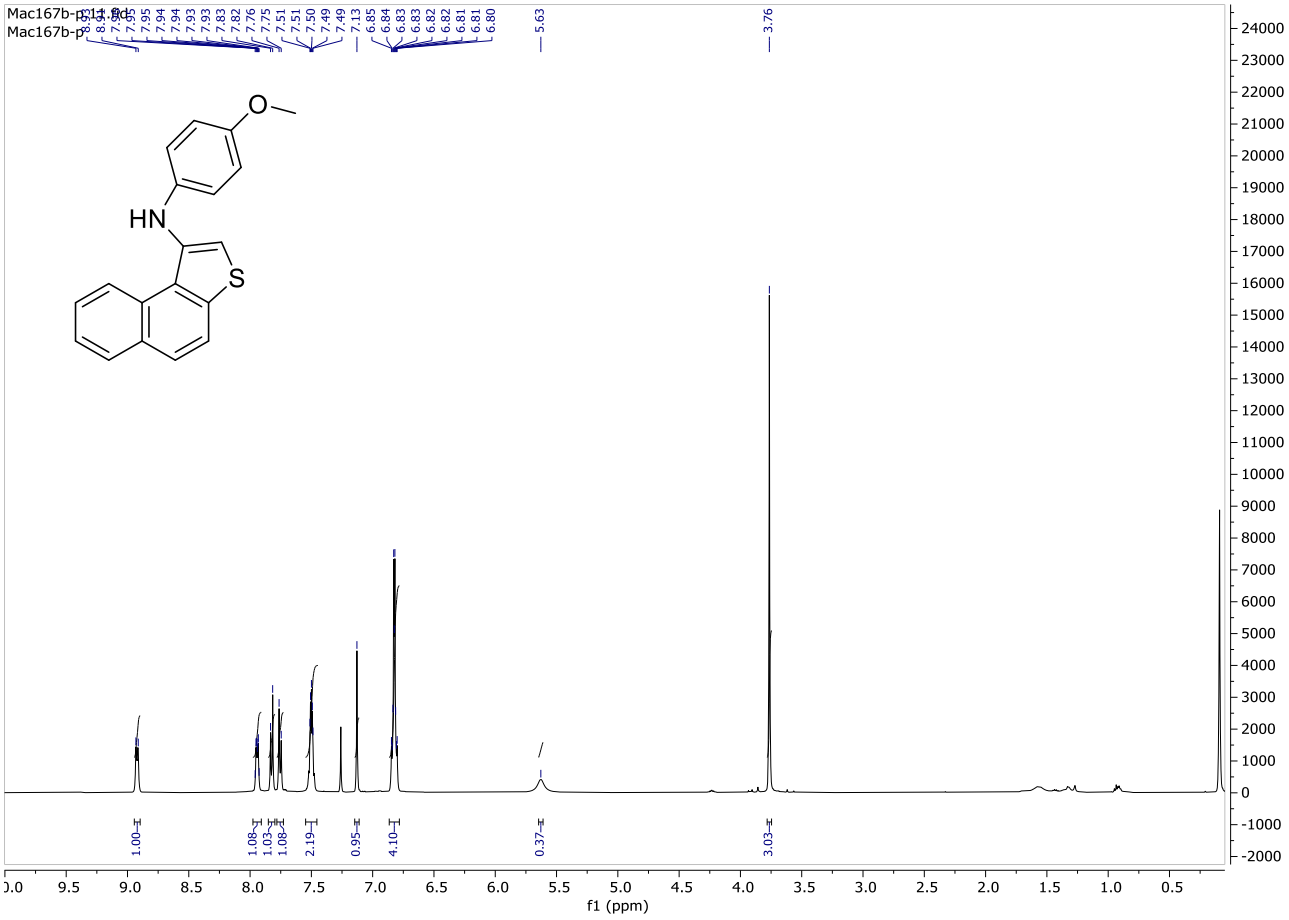


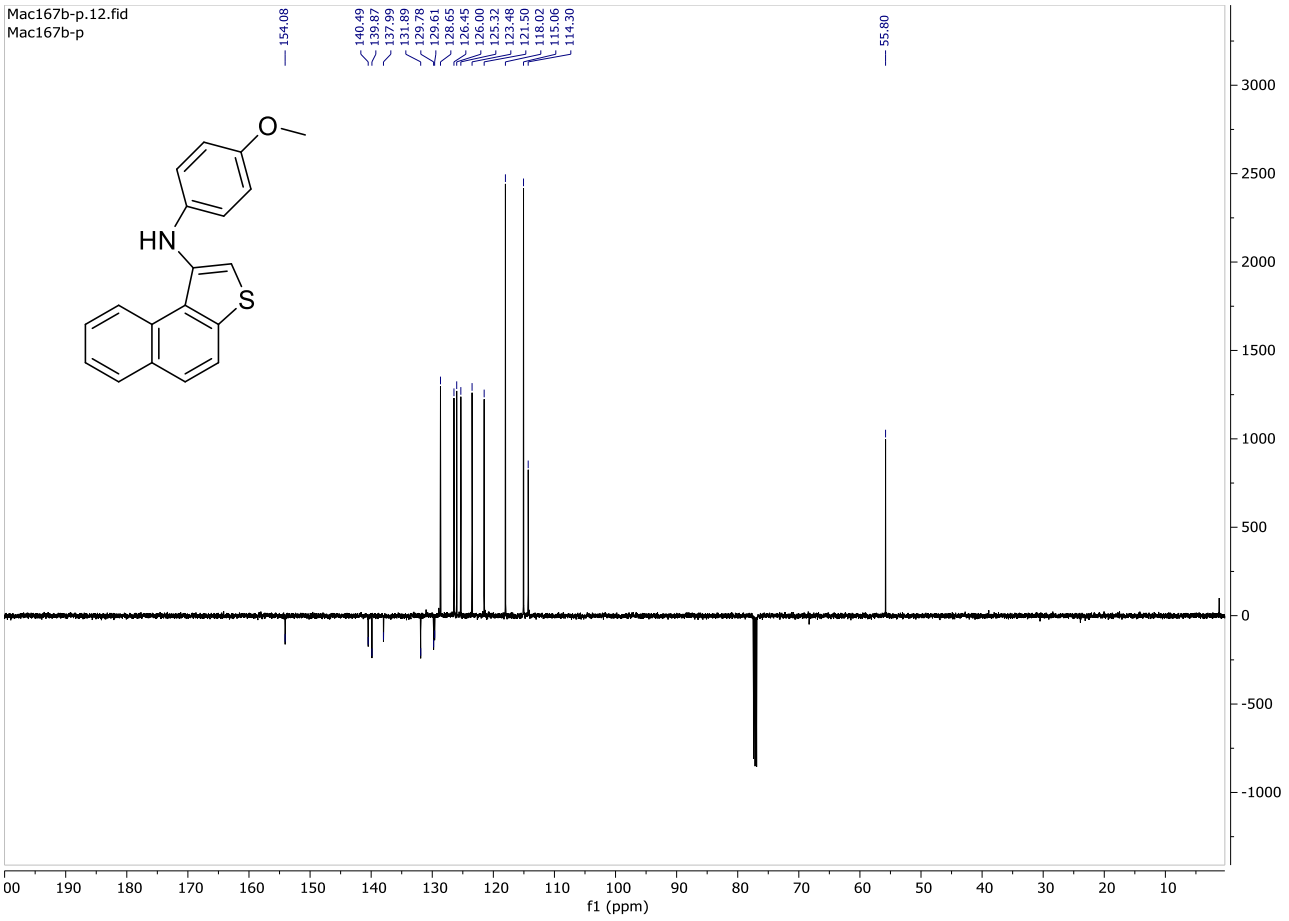
_N_-(m-Tolyl)naphtho[2,1-b]thiophen-1-amine (3ab) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)



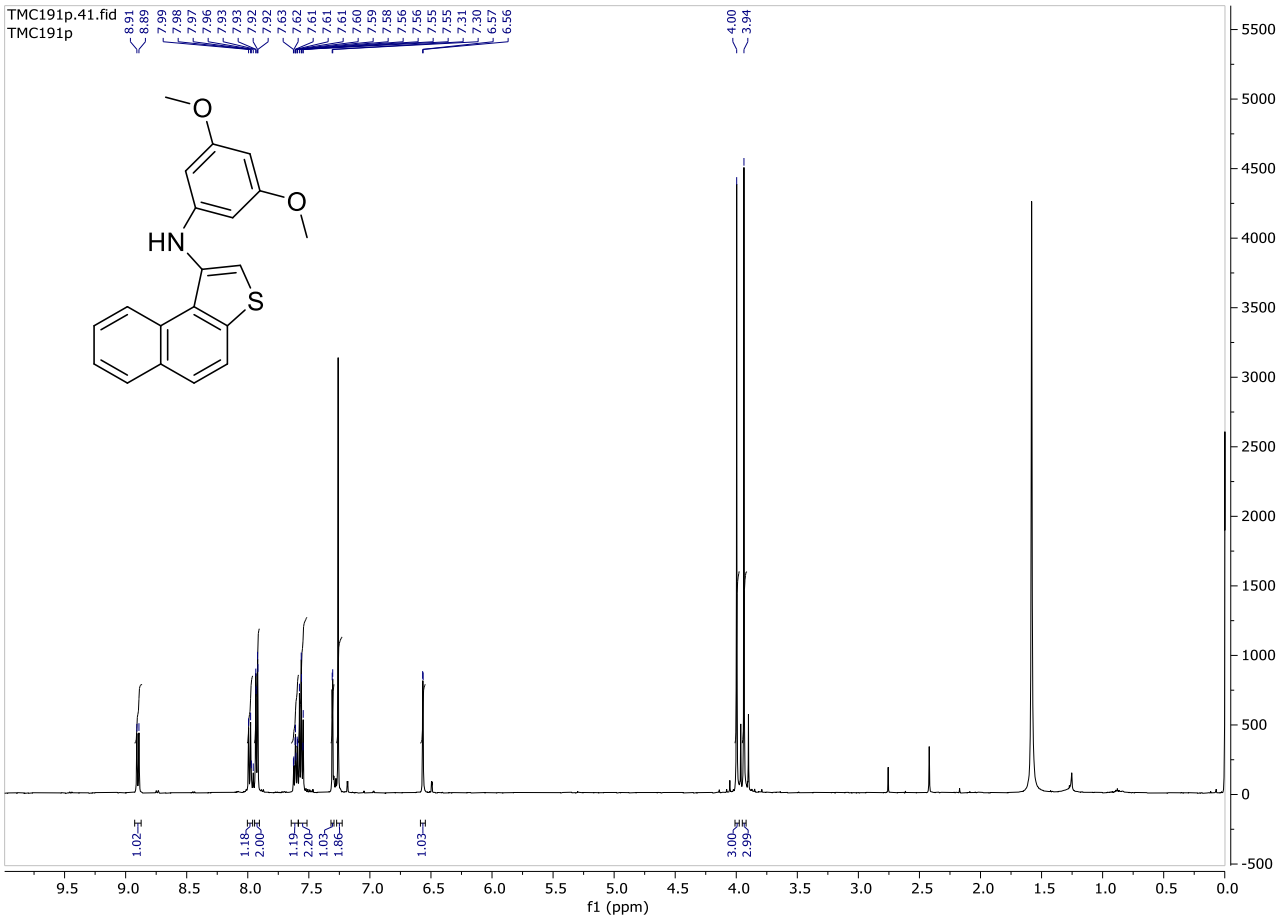


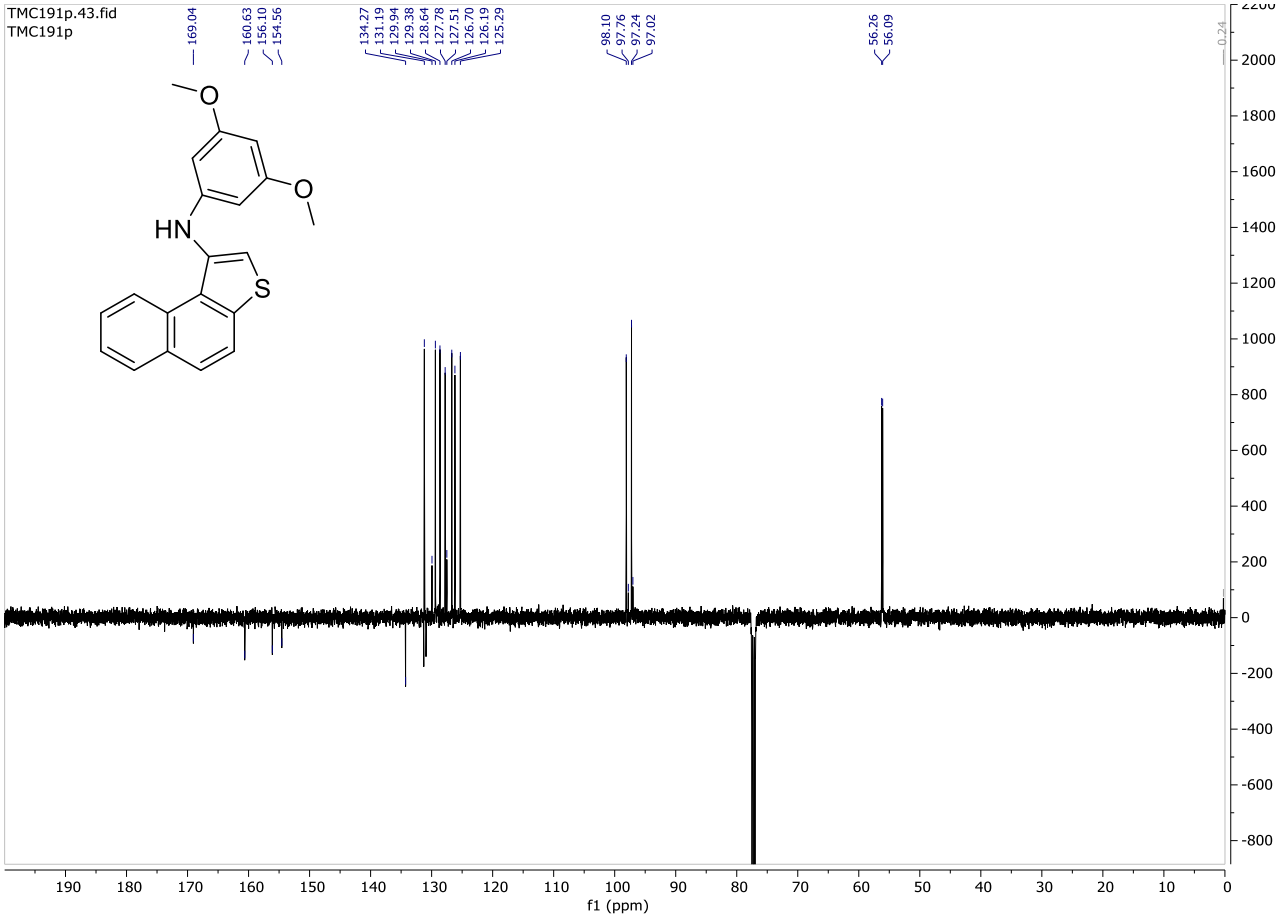
***N*-(4-Methoxyphenyl)naphtho[2,1-b]thiophen-1-amine (3ac) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)**



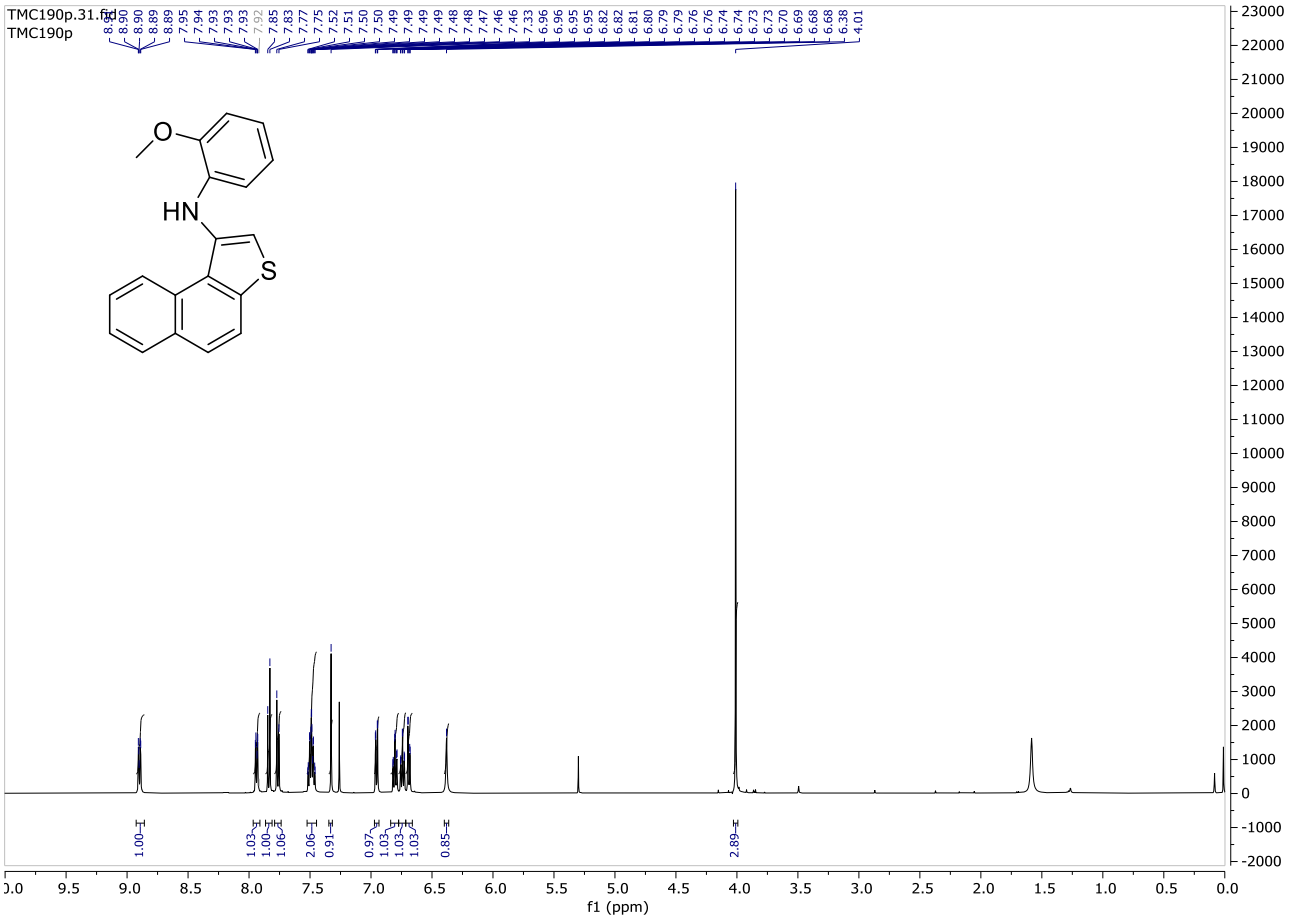


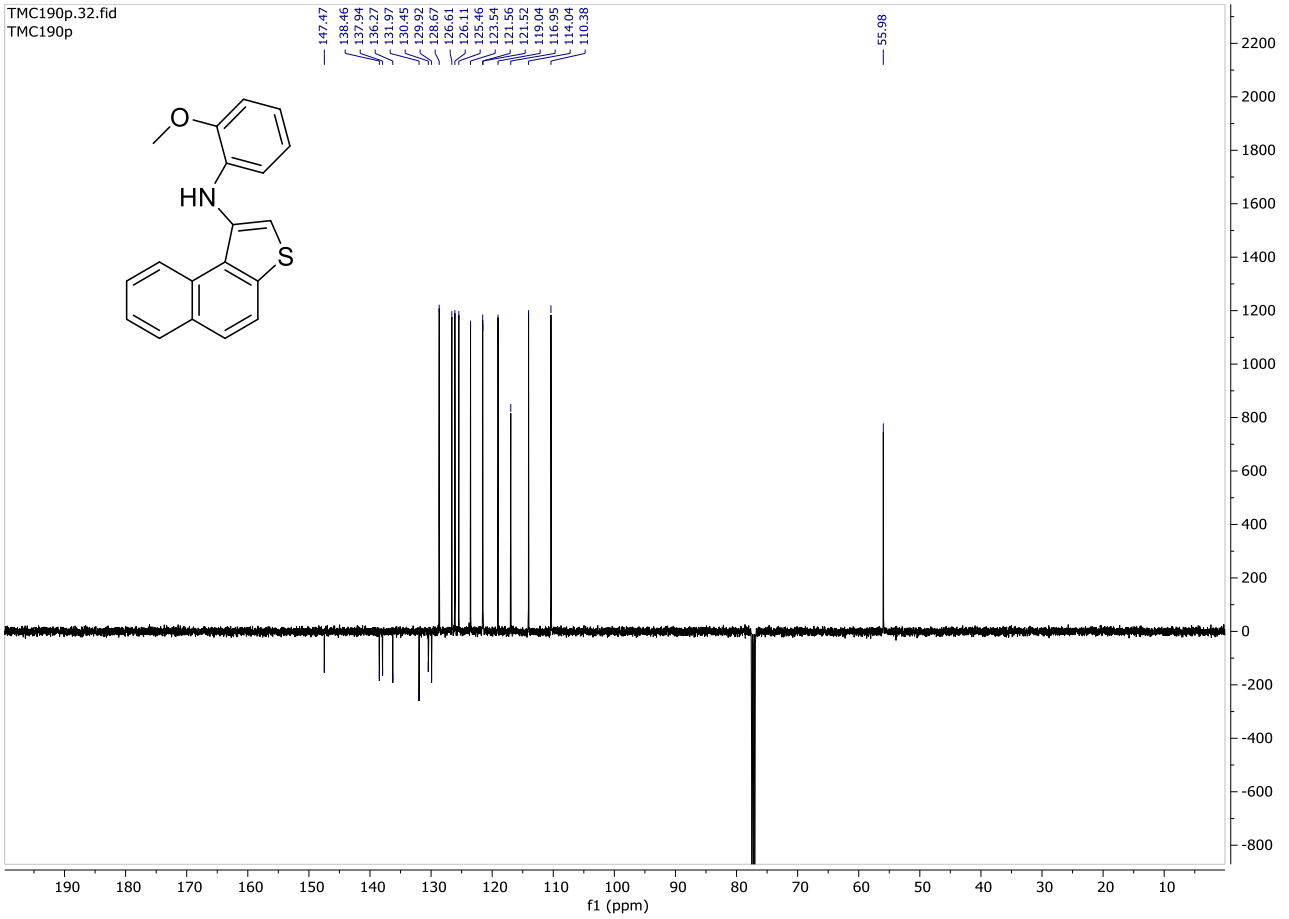
***N*-(3,5-dimethoxyphenyl)naphtho[2,1-b]thiophen-1-amine (3ad) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)**



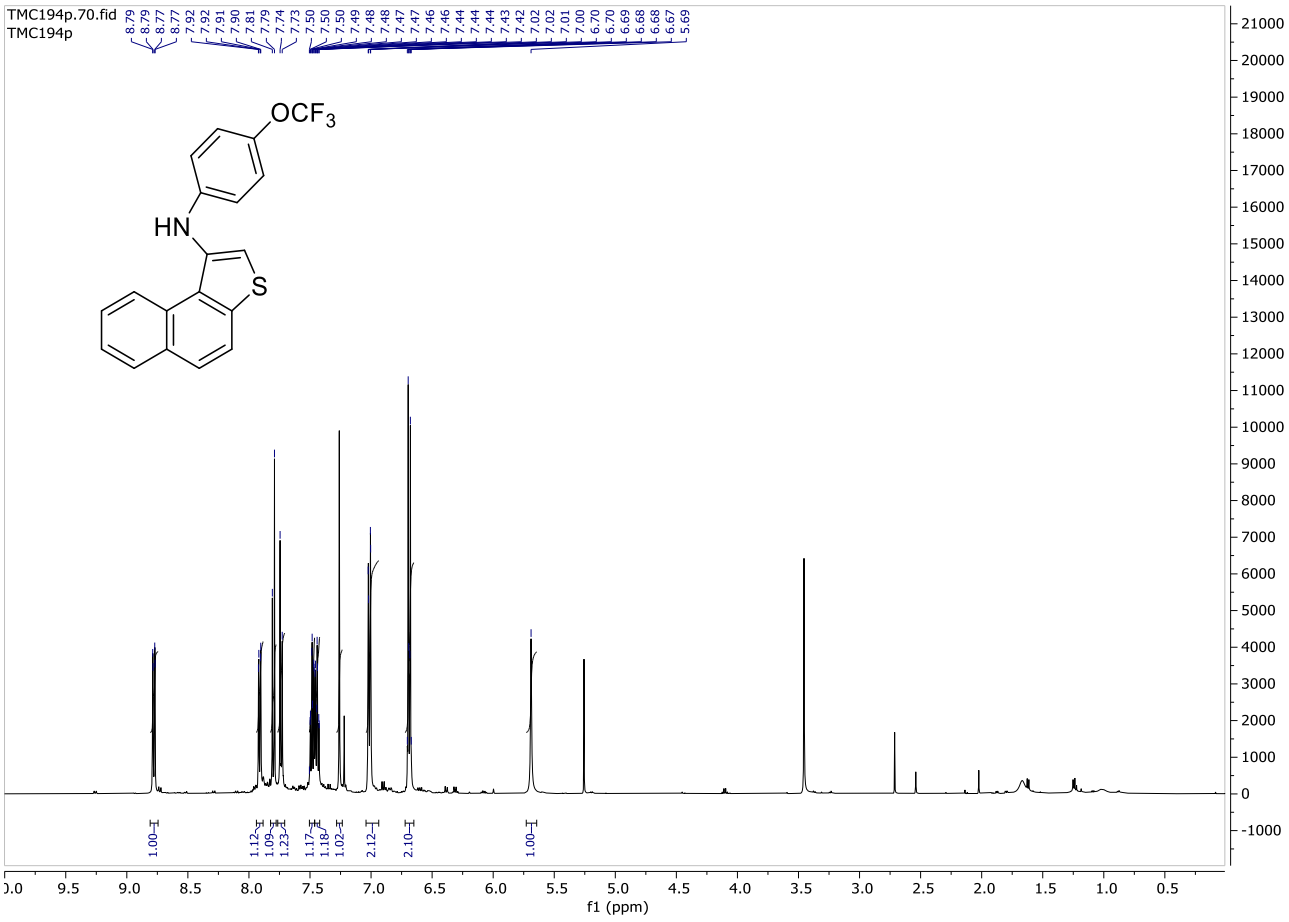


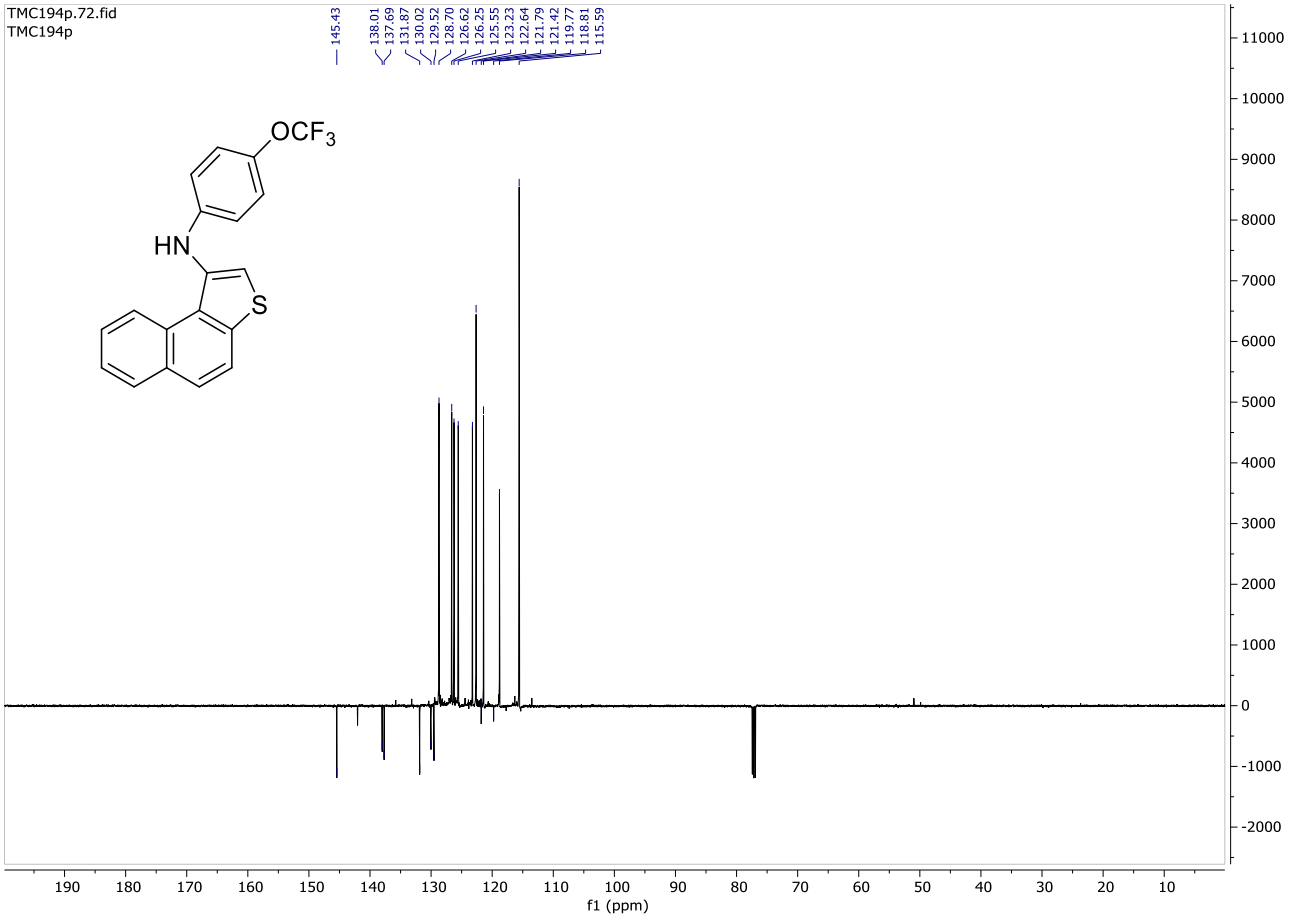
***N*-(2-Methoxyphenyl)naphtho[2,1-b]thiophen-1-amine (3ae) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)**

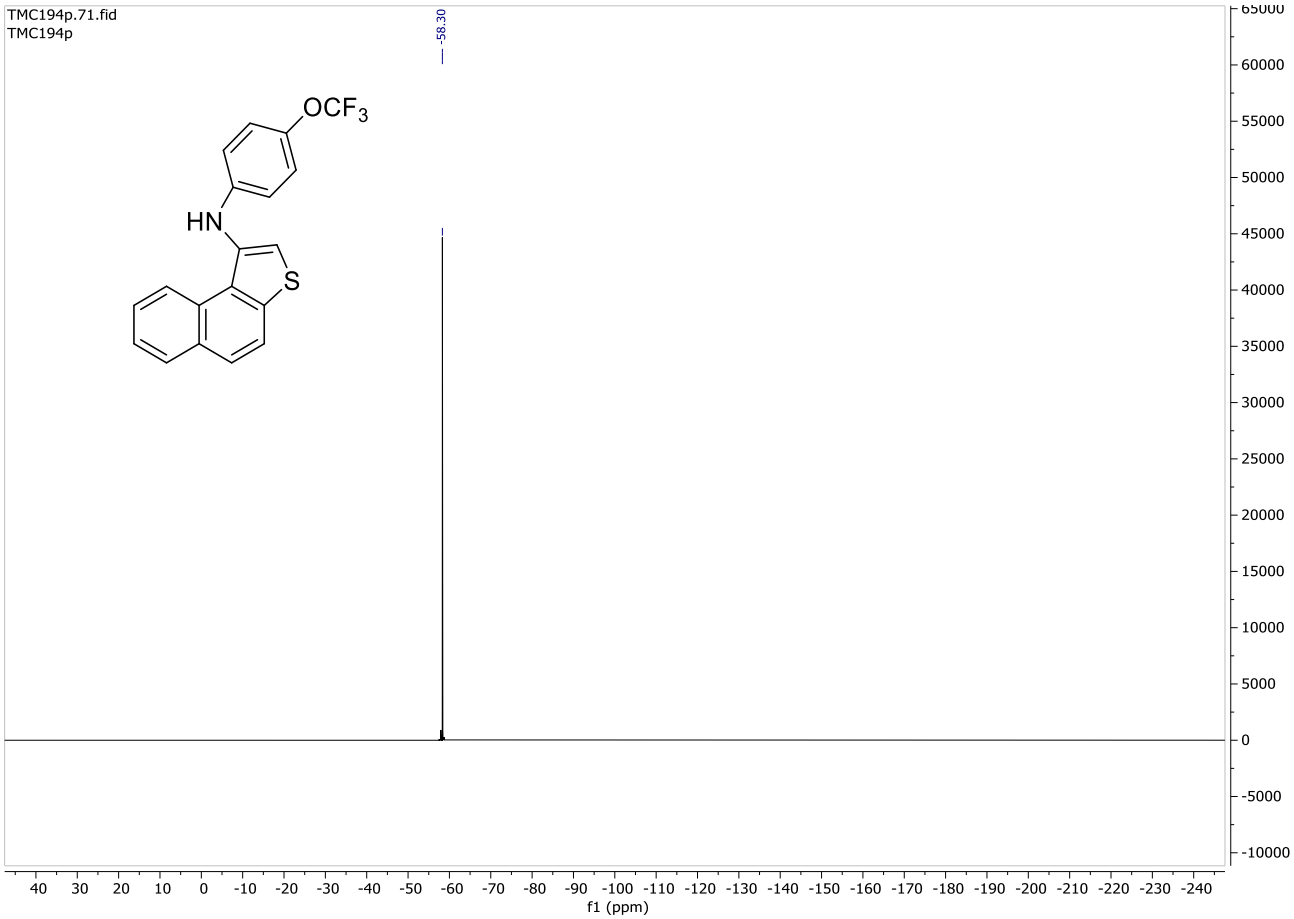




***N*-(4-(Trifluoromethoxy)phenyl)naphtho[2,1-b]thiophen-1-amine (3af) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)**



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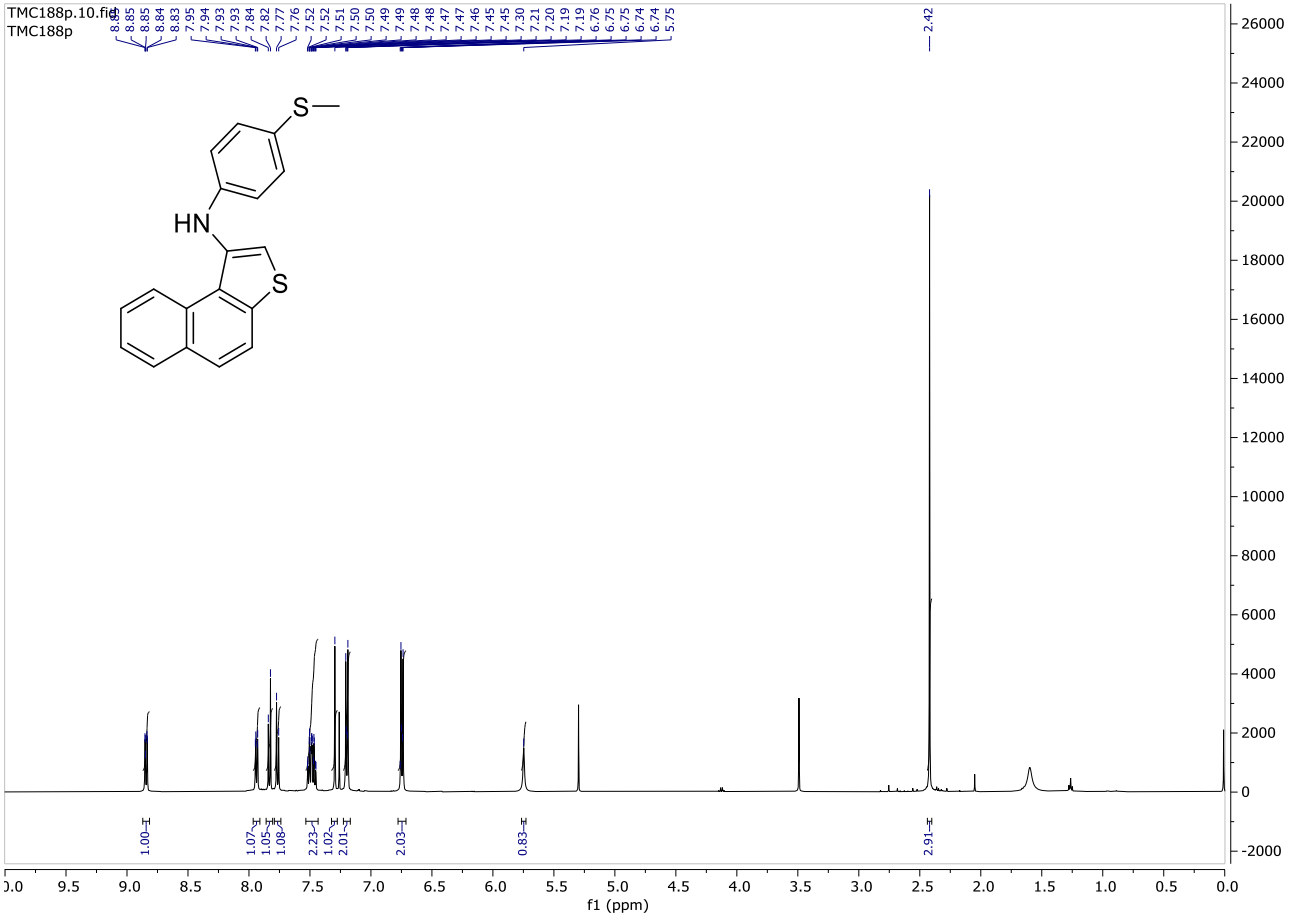
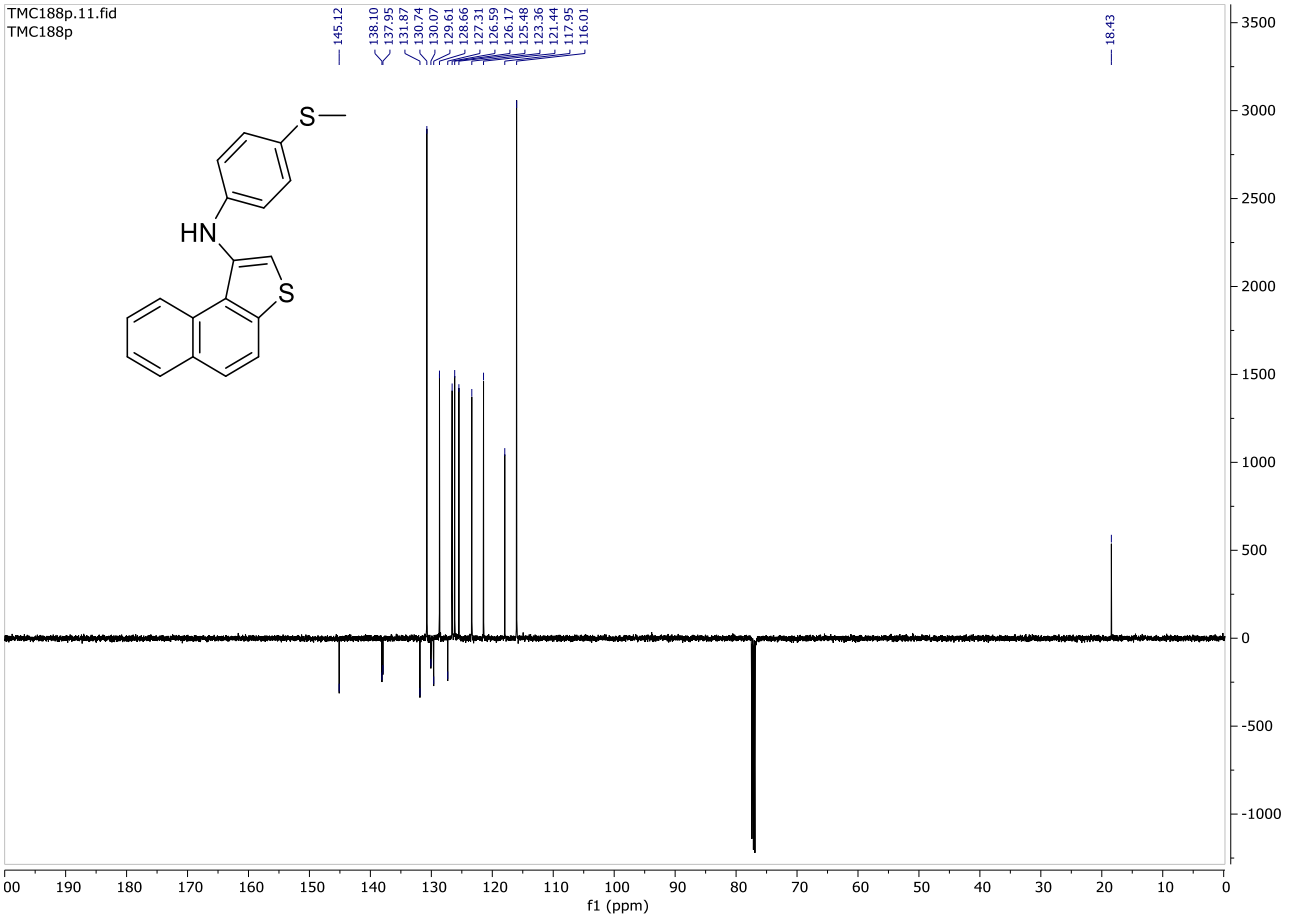
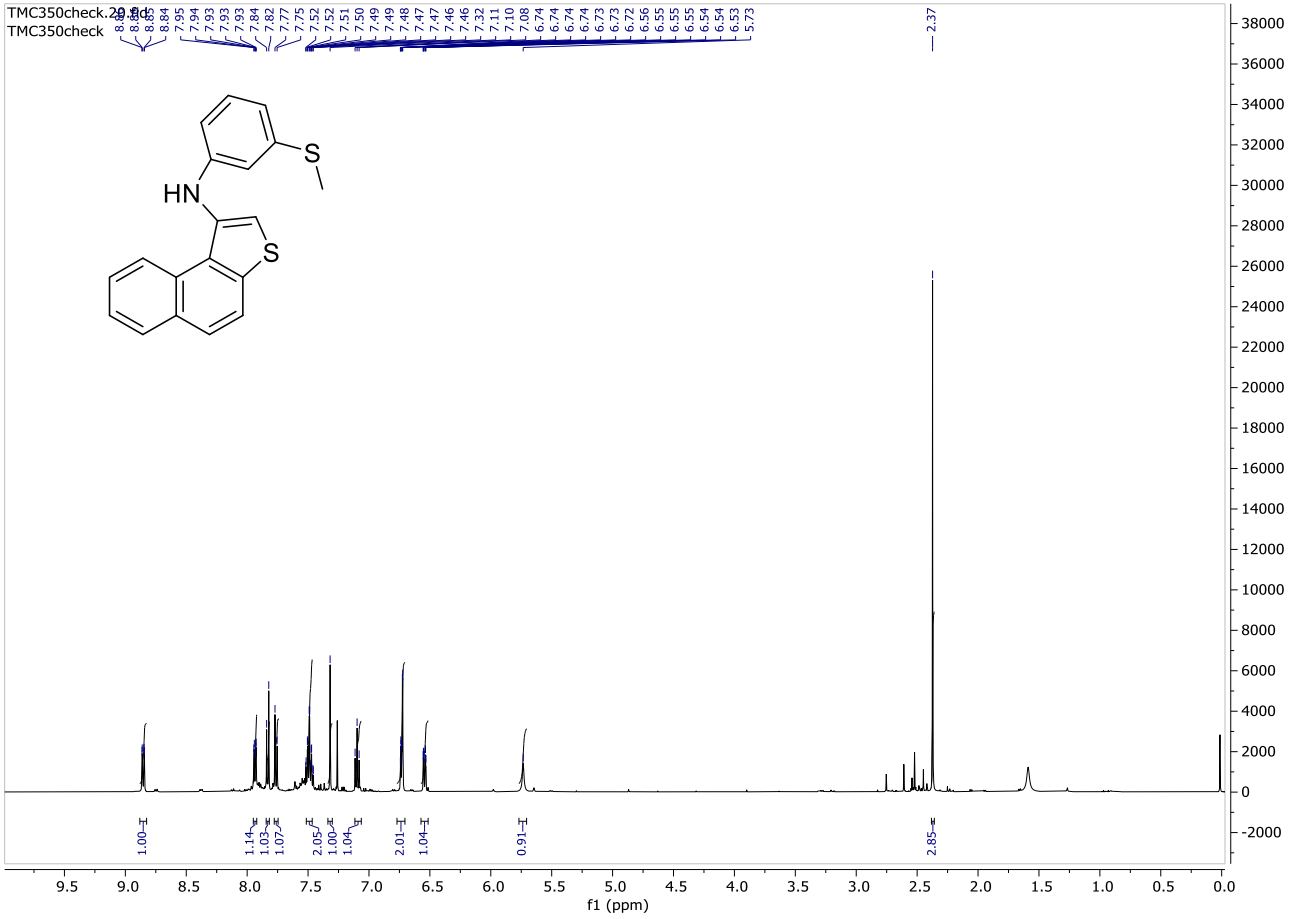
-5000
-10000
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

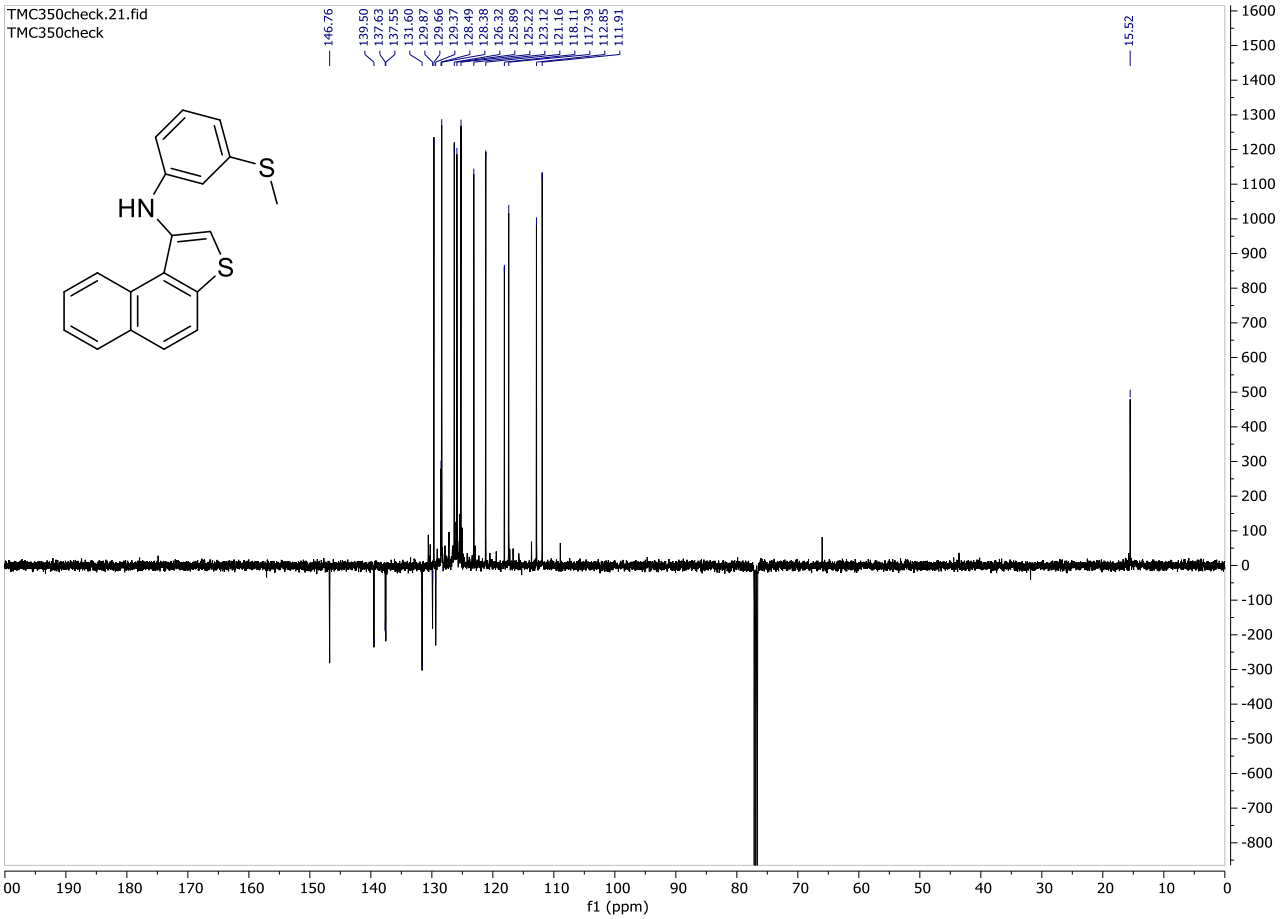
***N*-(4-(Methylthio)phenyl)naphtho[2,1-b]thiophen-1-amine (3ag) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)**



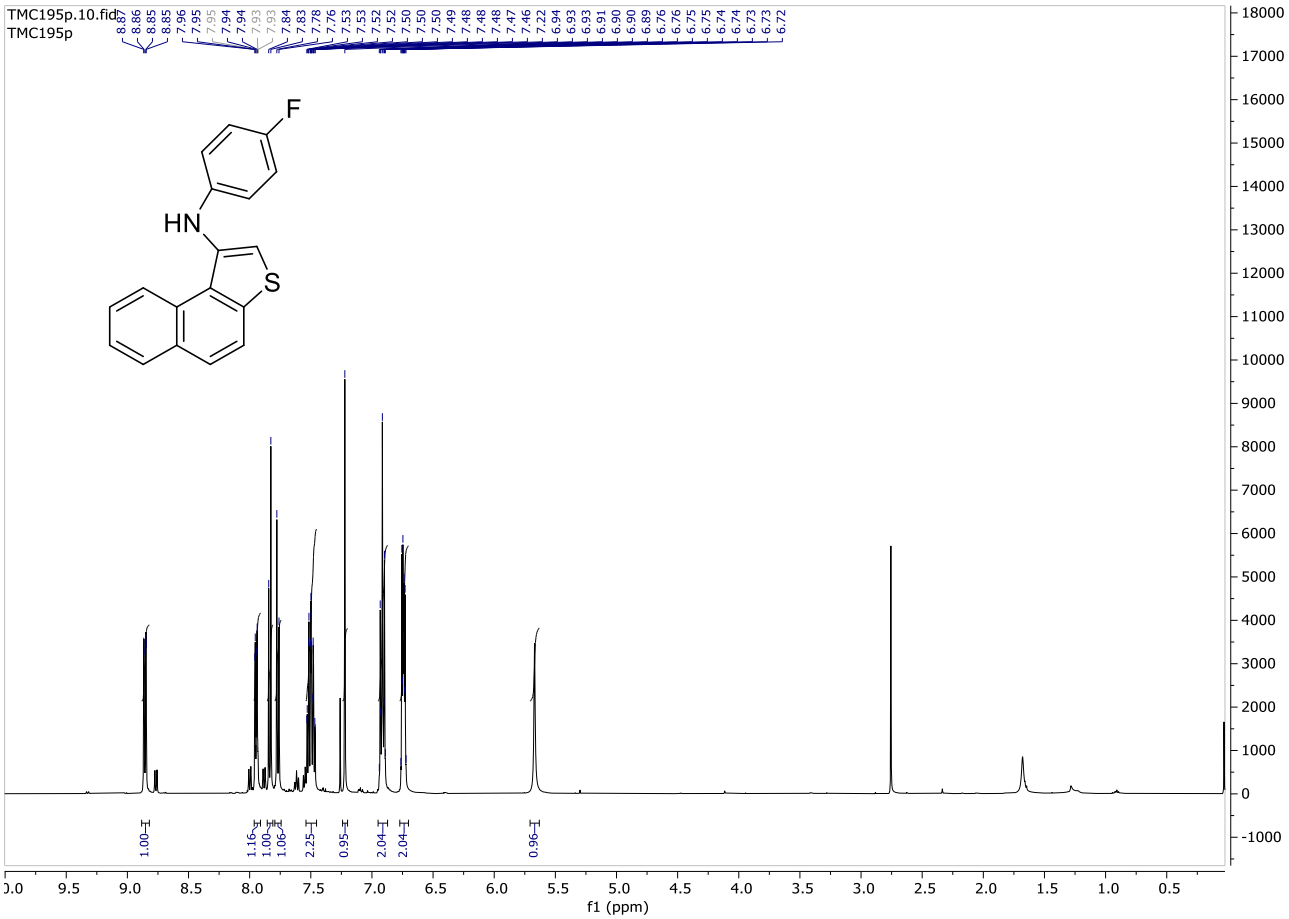


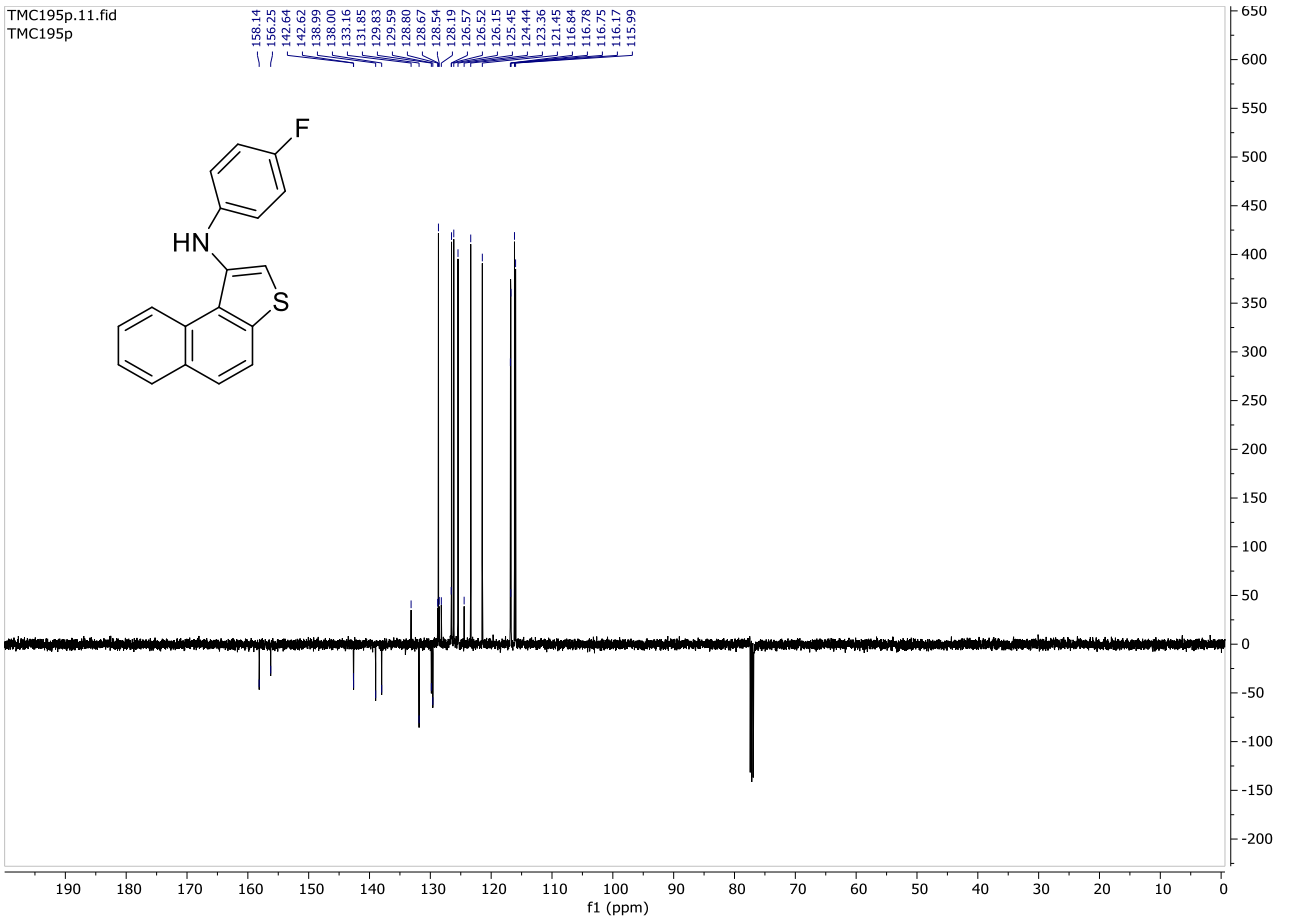
***N*-(3-(Methylthio)phenyl)naphtho[2,1-b]thiophen-1-amine (3ah) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)**

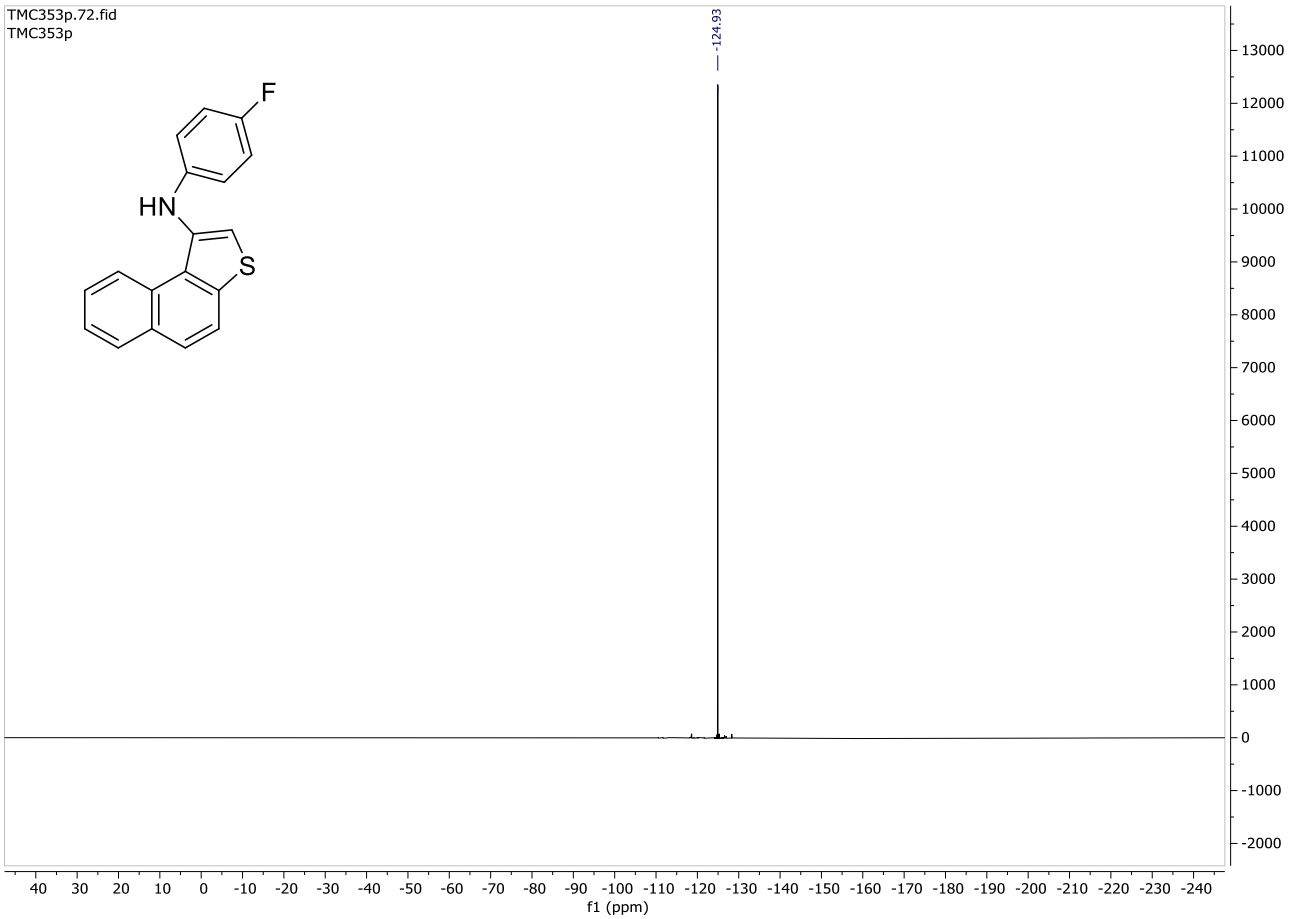




***N*-(4-Fluorophenyl)naphtho[2,1-b]thiophen-1-amine (3ai) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)**



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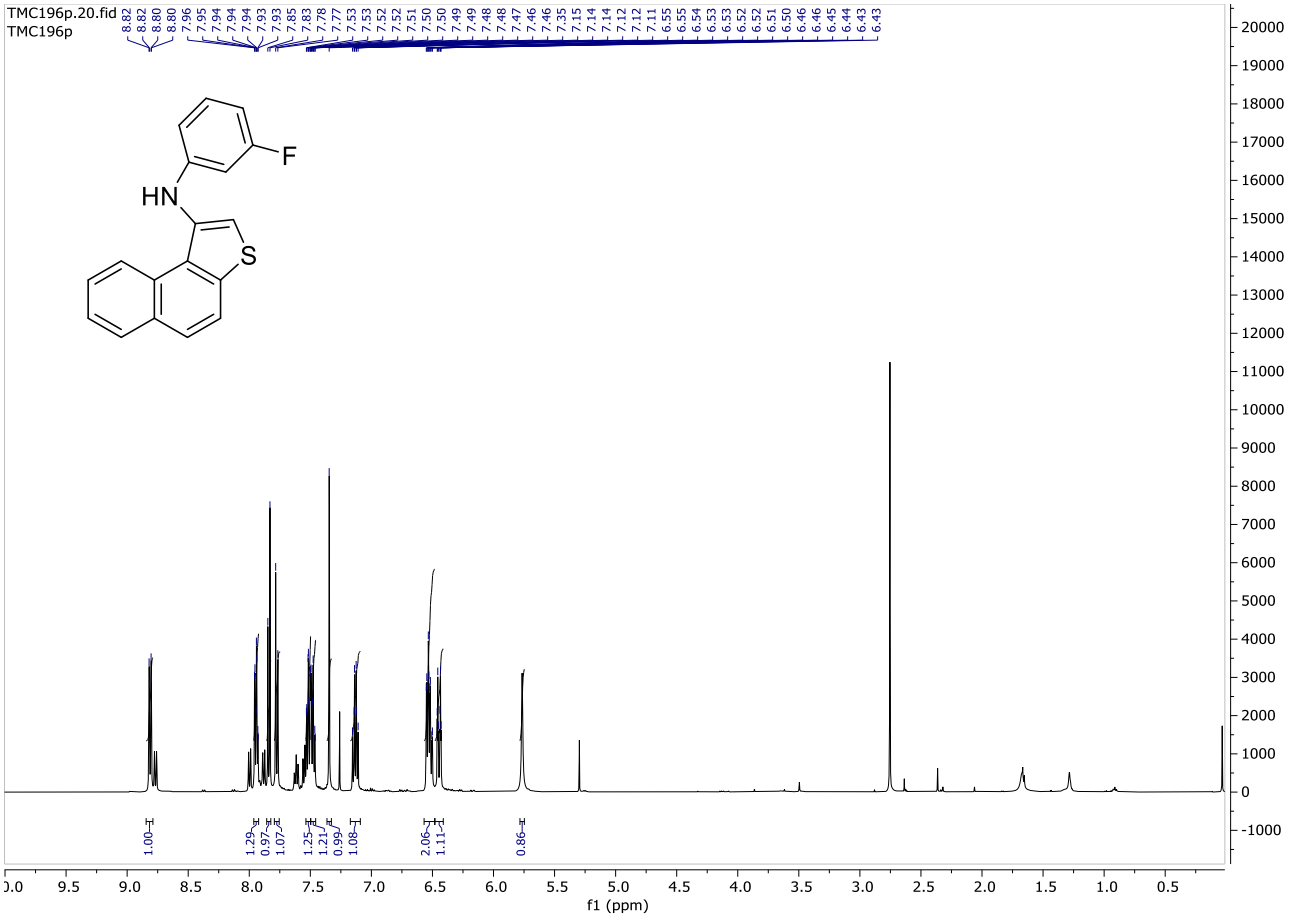
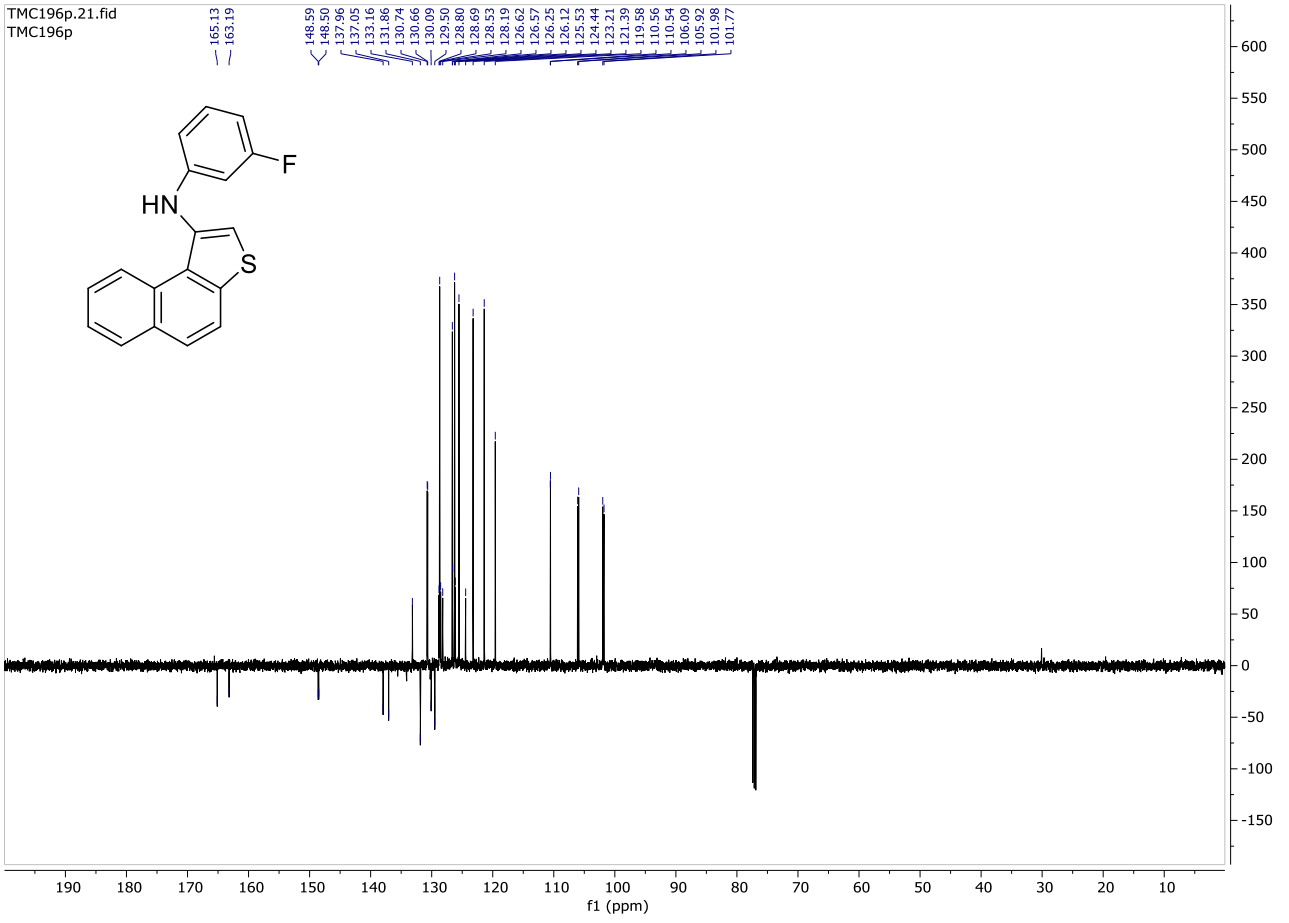
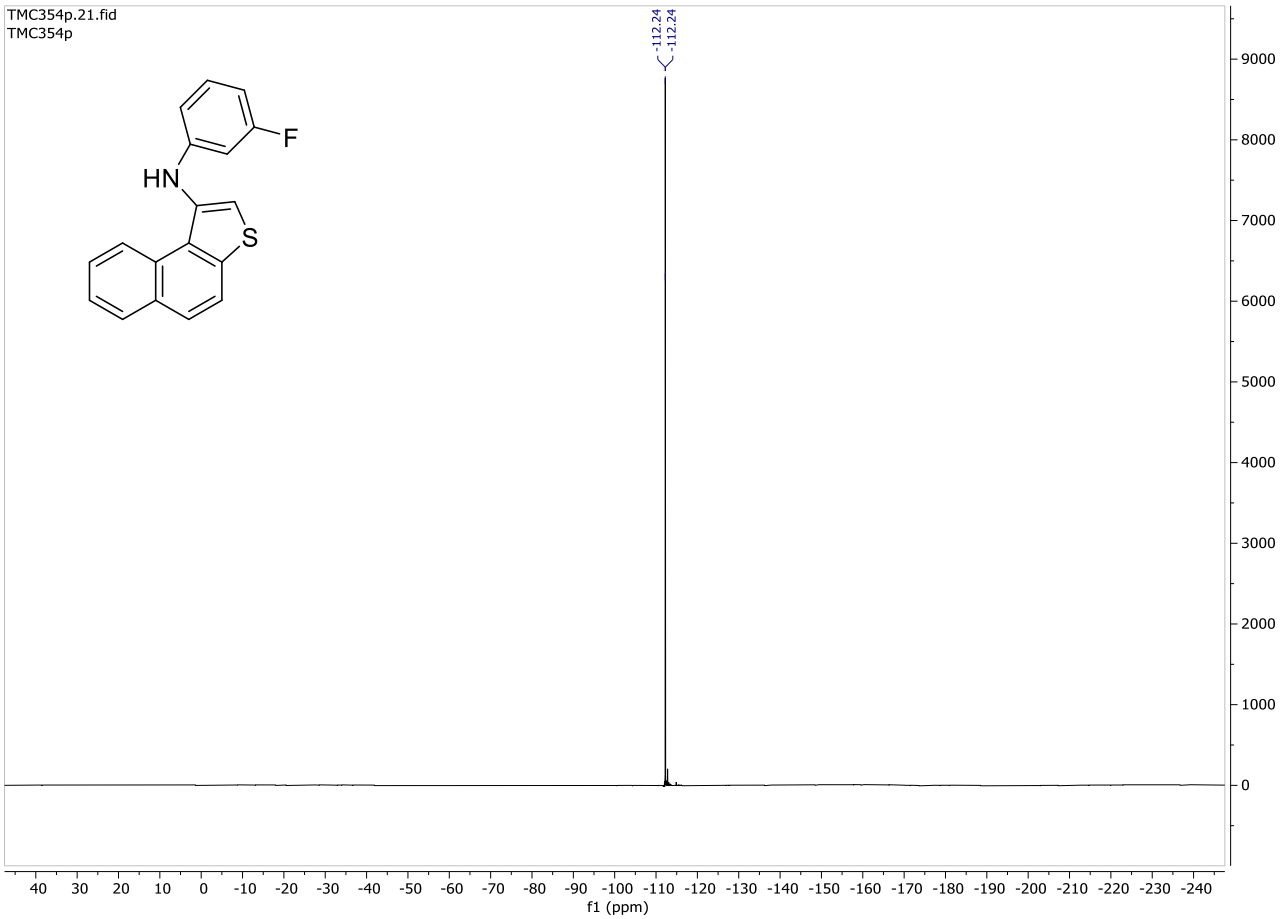
f1 (ppm)

***N*-(3-Fluorophenyl)naphtho[2,1-b]thiophen-1-amine (3aj) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)**



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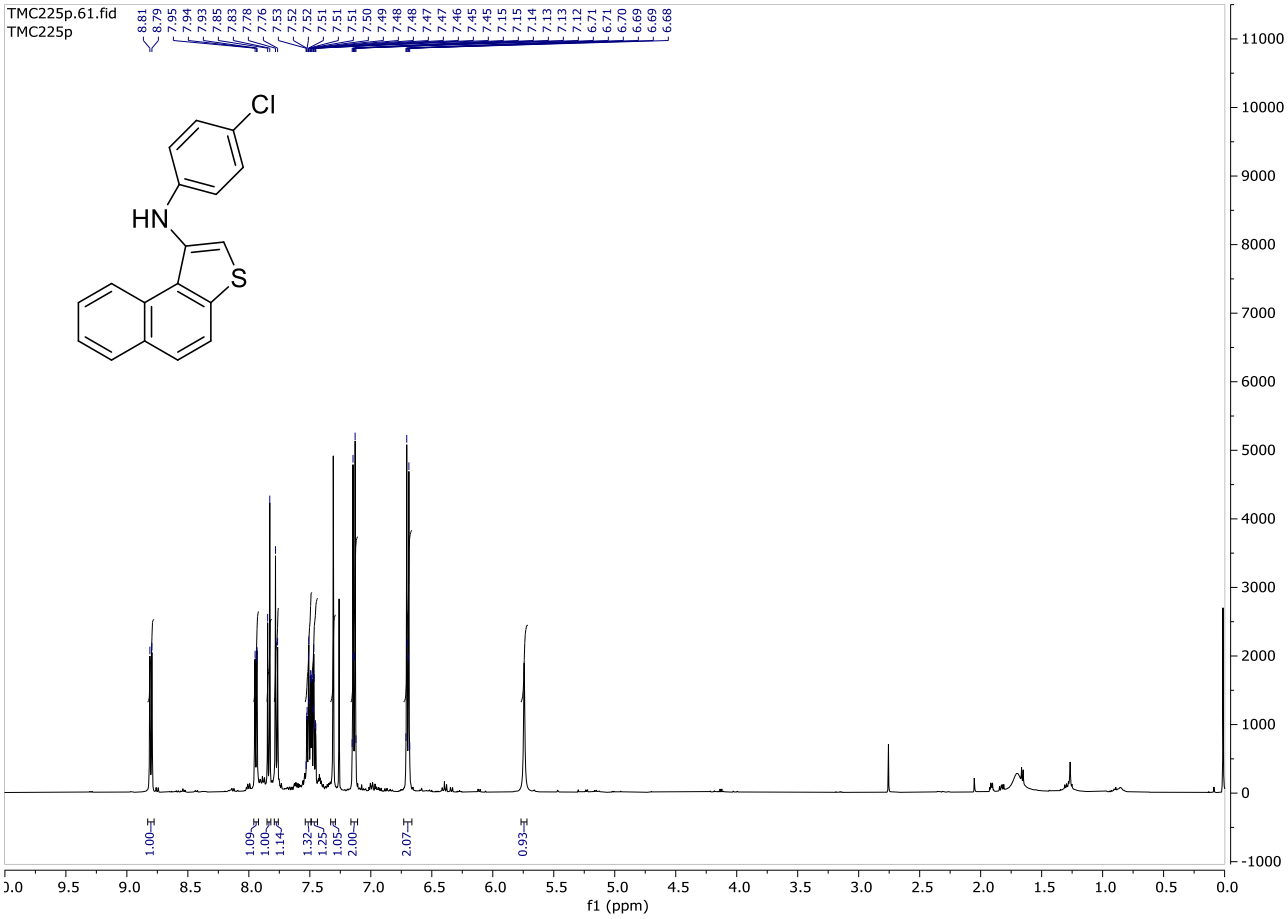
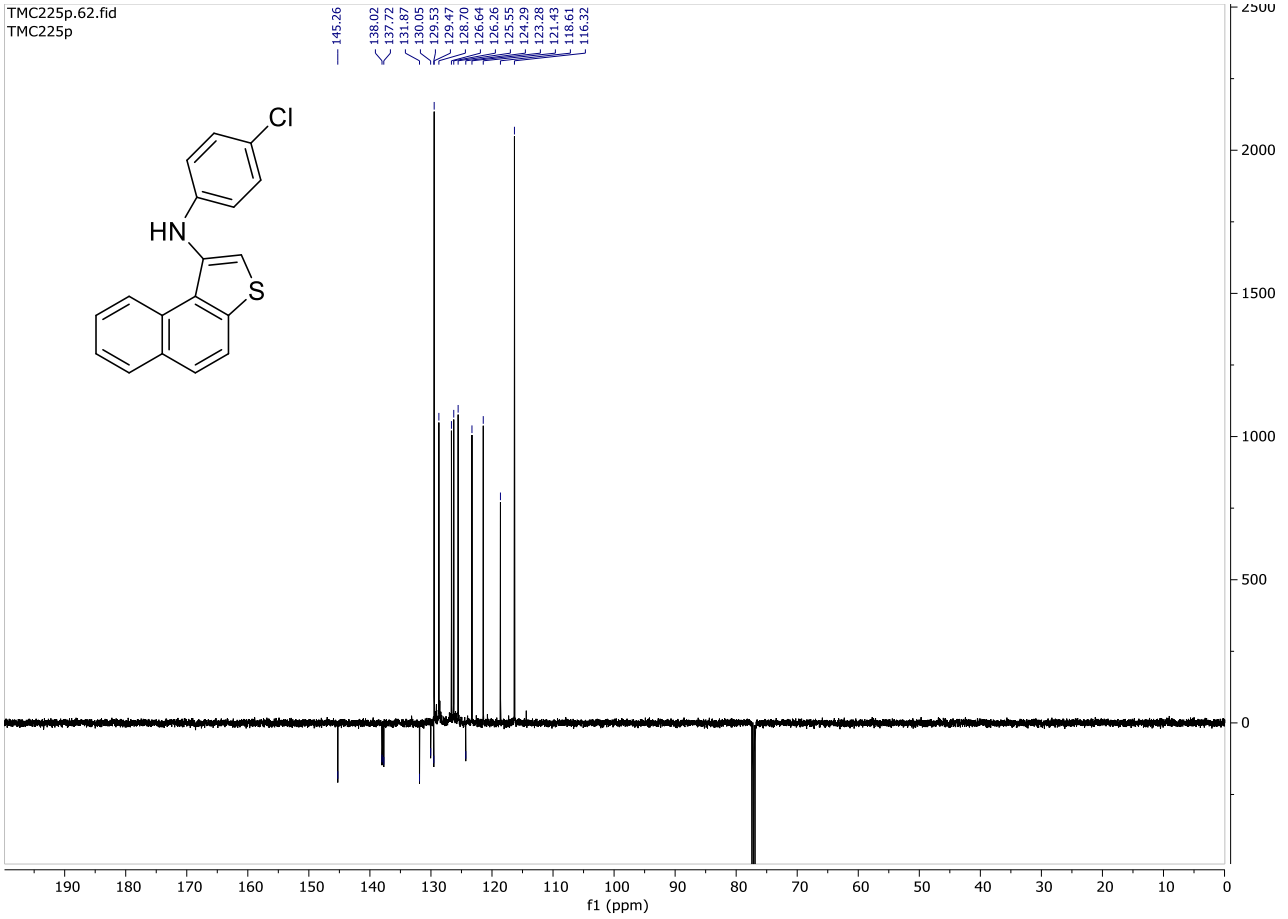
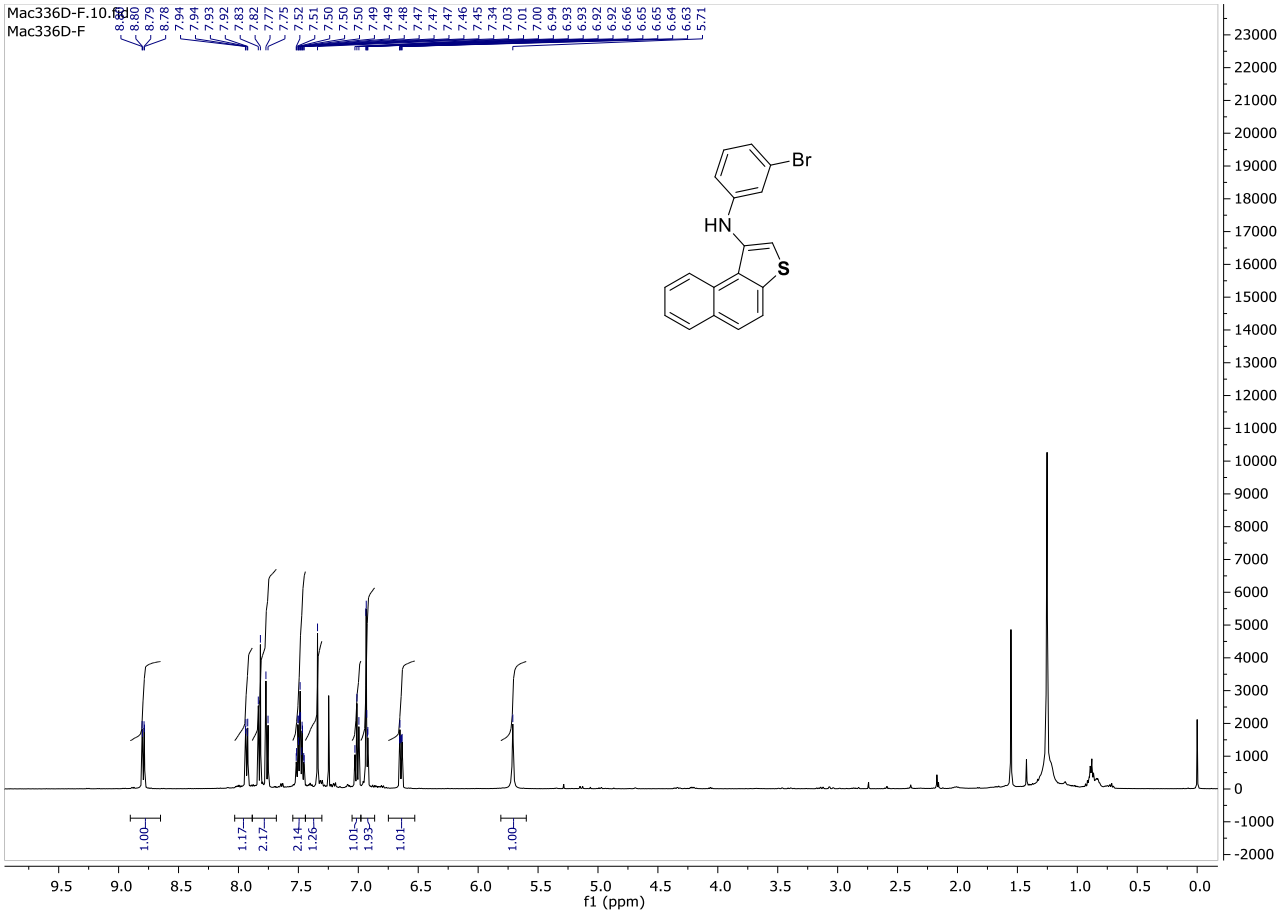
2000
1000
0
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

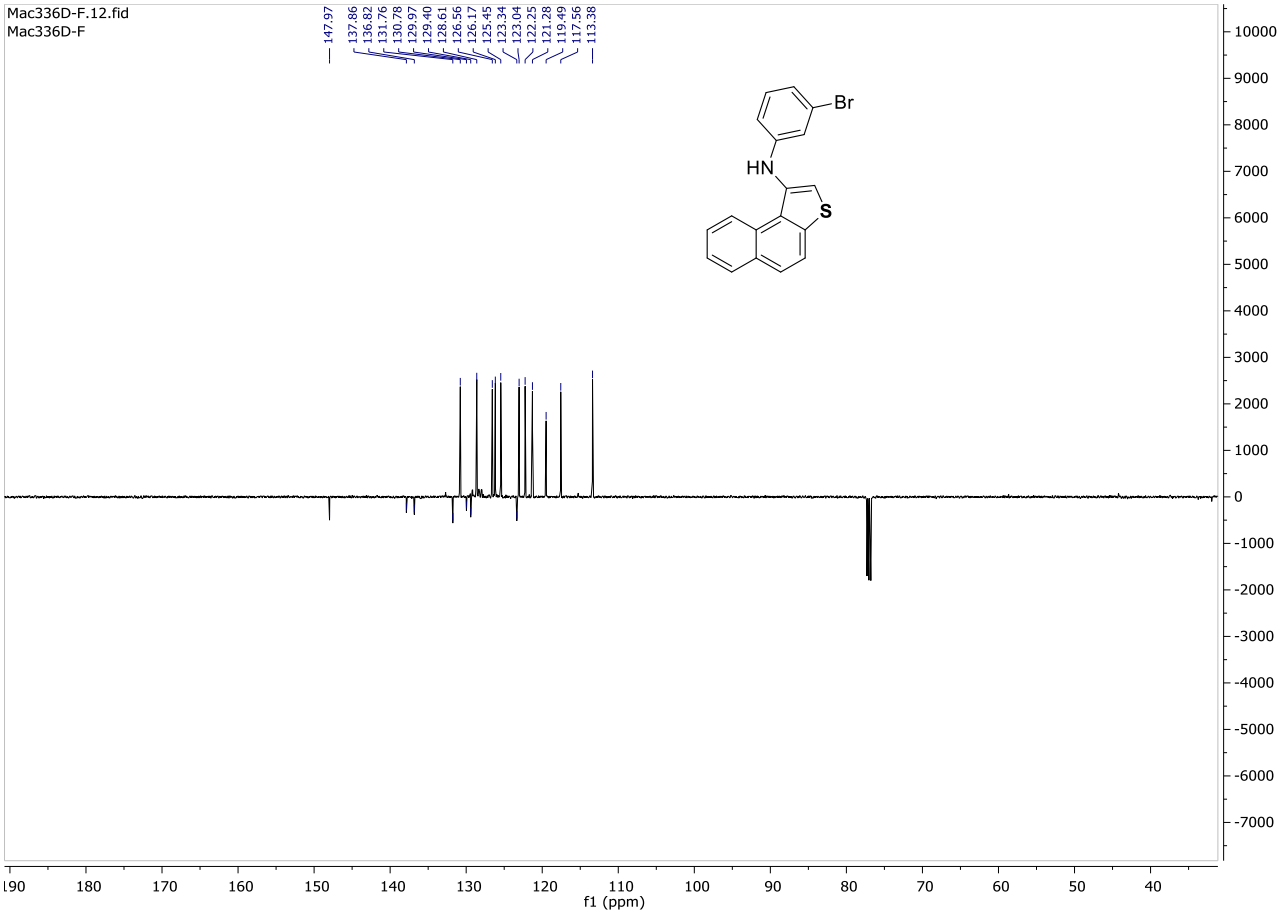
N-(4-Chlorophenyl)naphtho[2,1-b]thiophen-1-amine (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)



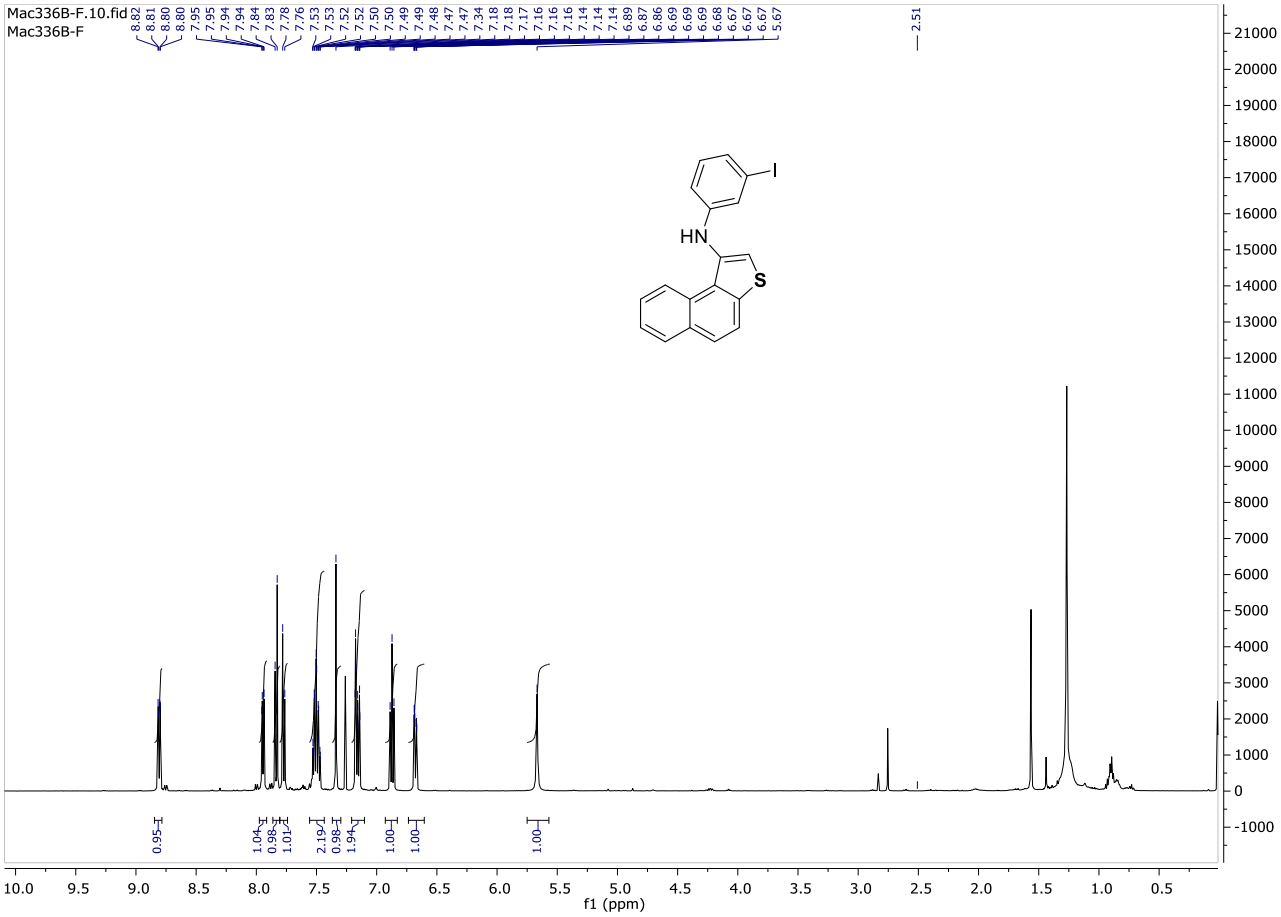


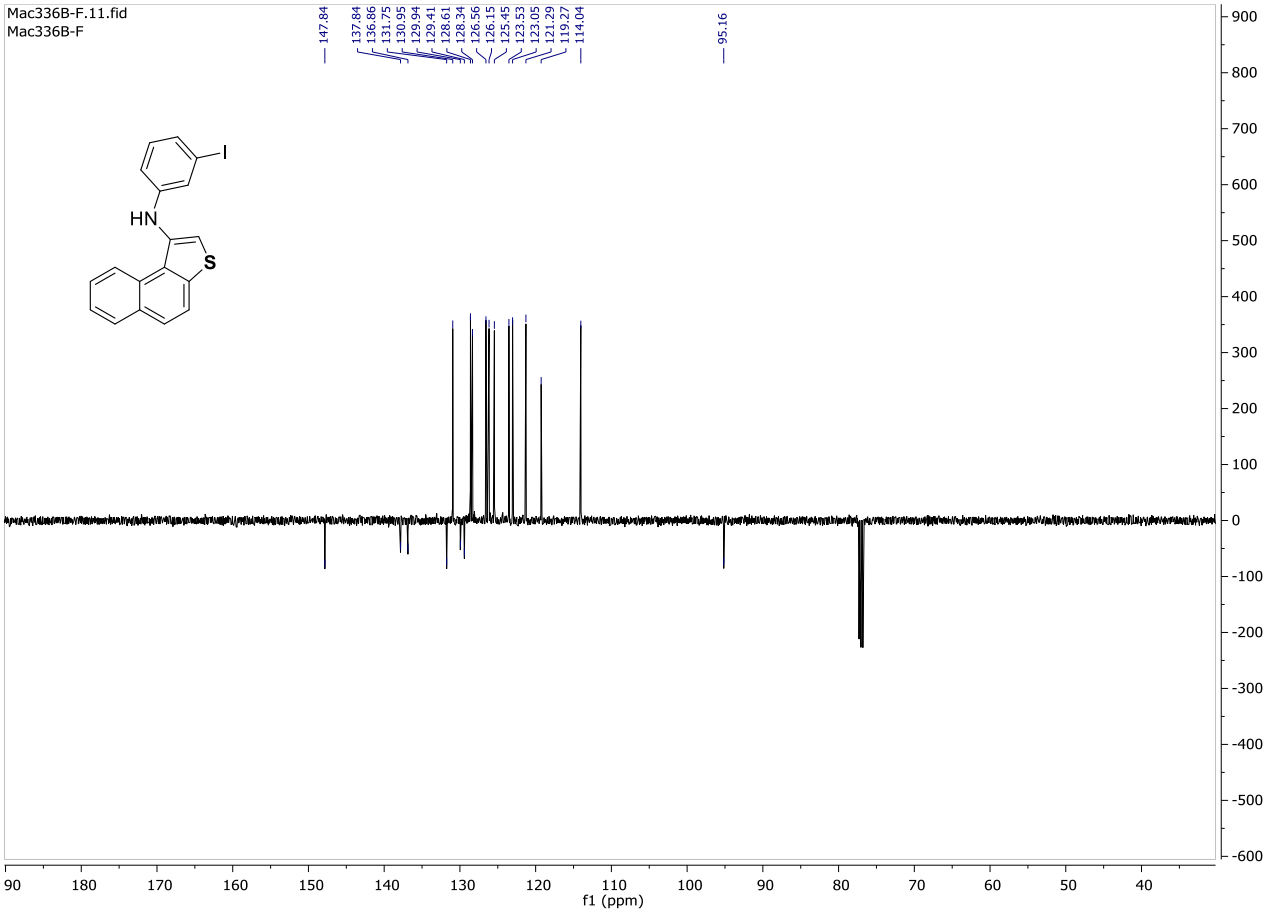
***N*-(3-Bromophenyl)naphtho[2,1-b]thiophen-1-amine (3al) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)**



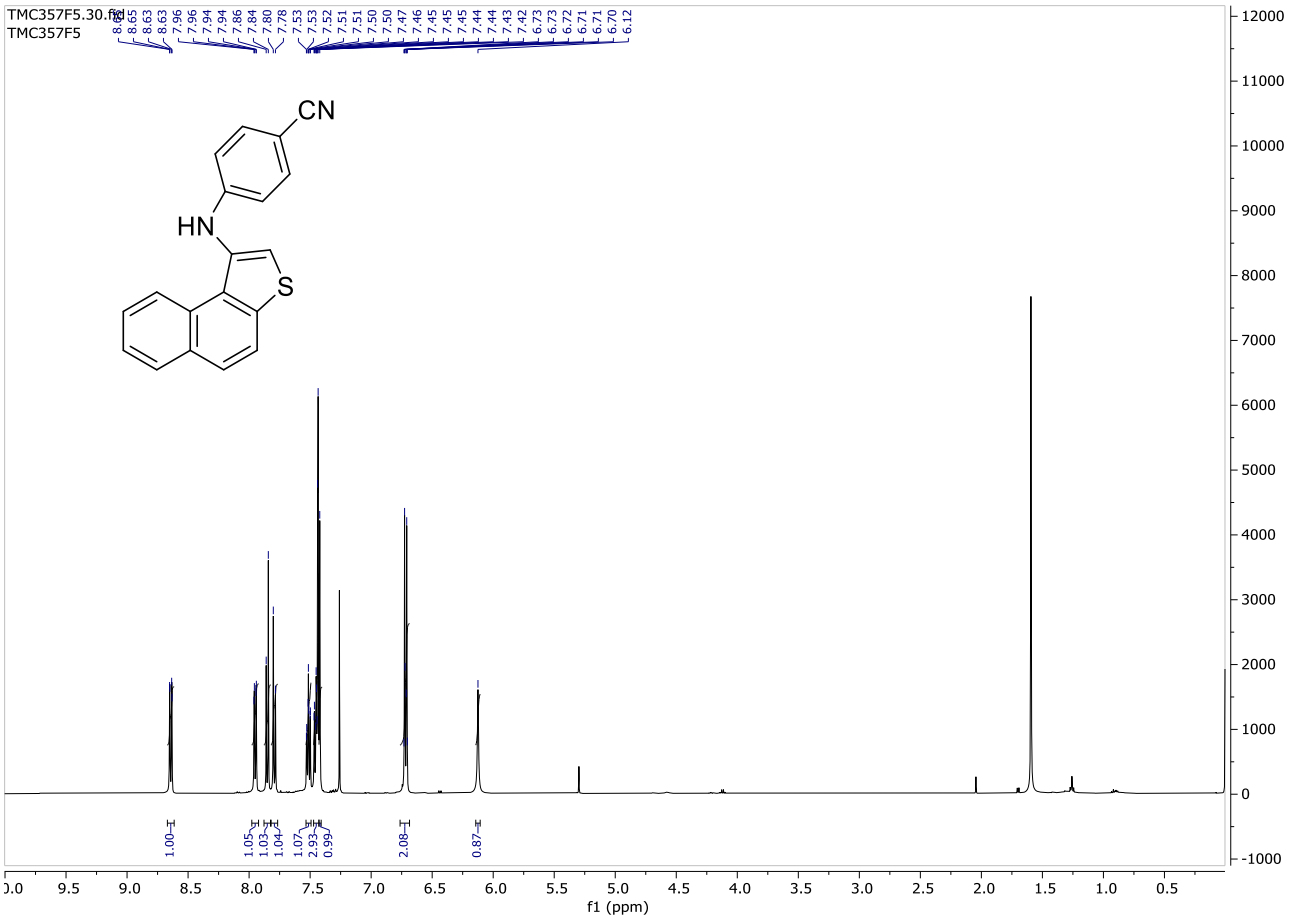


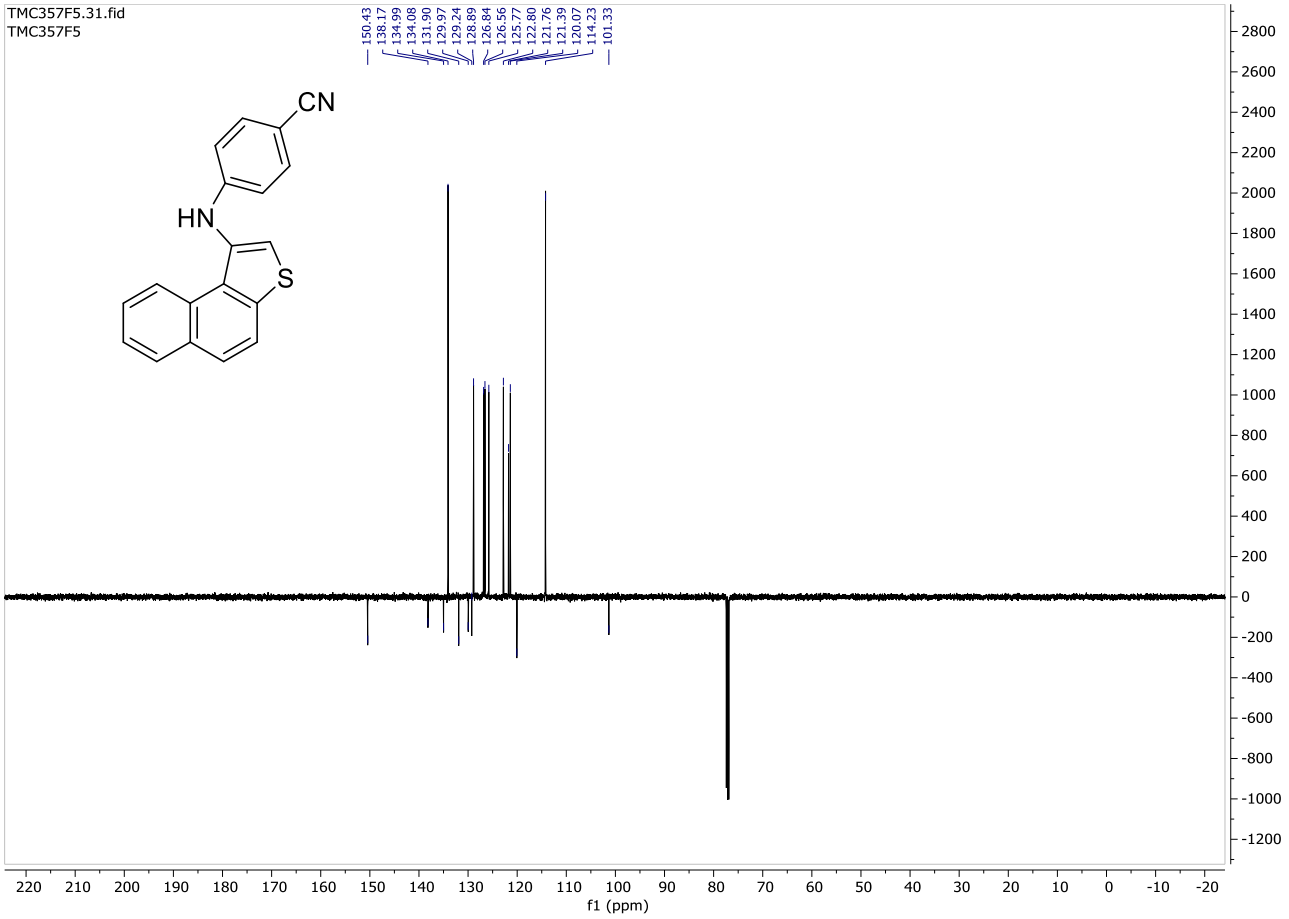
***N*-(3-iodophenyl)naphtho[2,1-b]thiophen-1-amine (3am) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)**



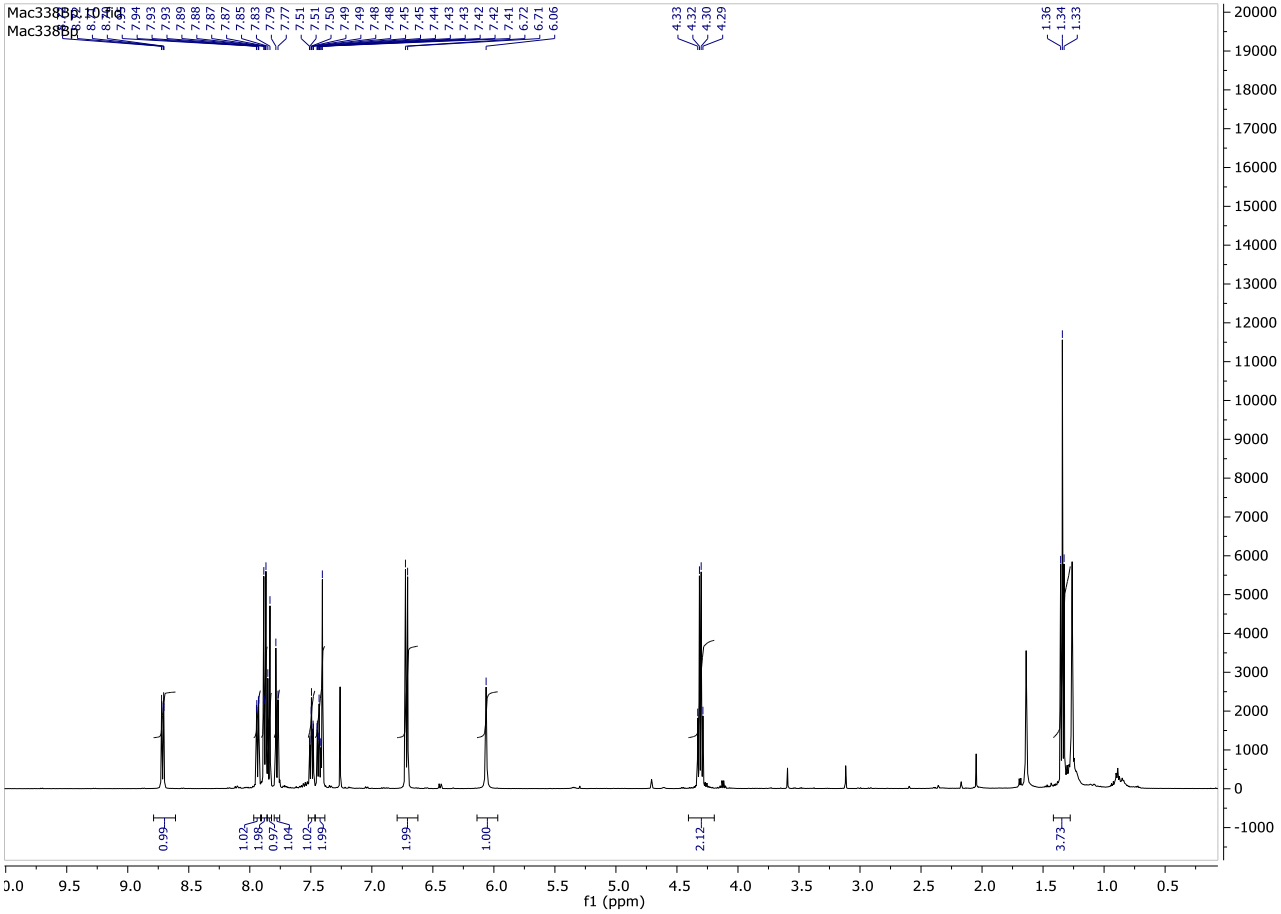


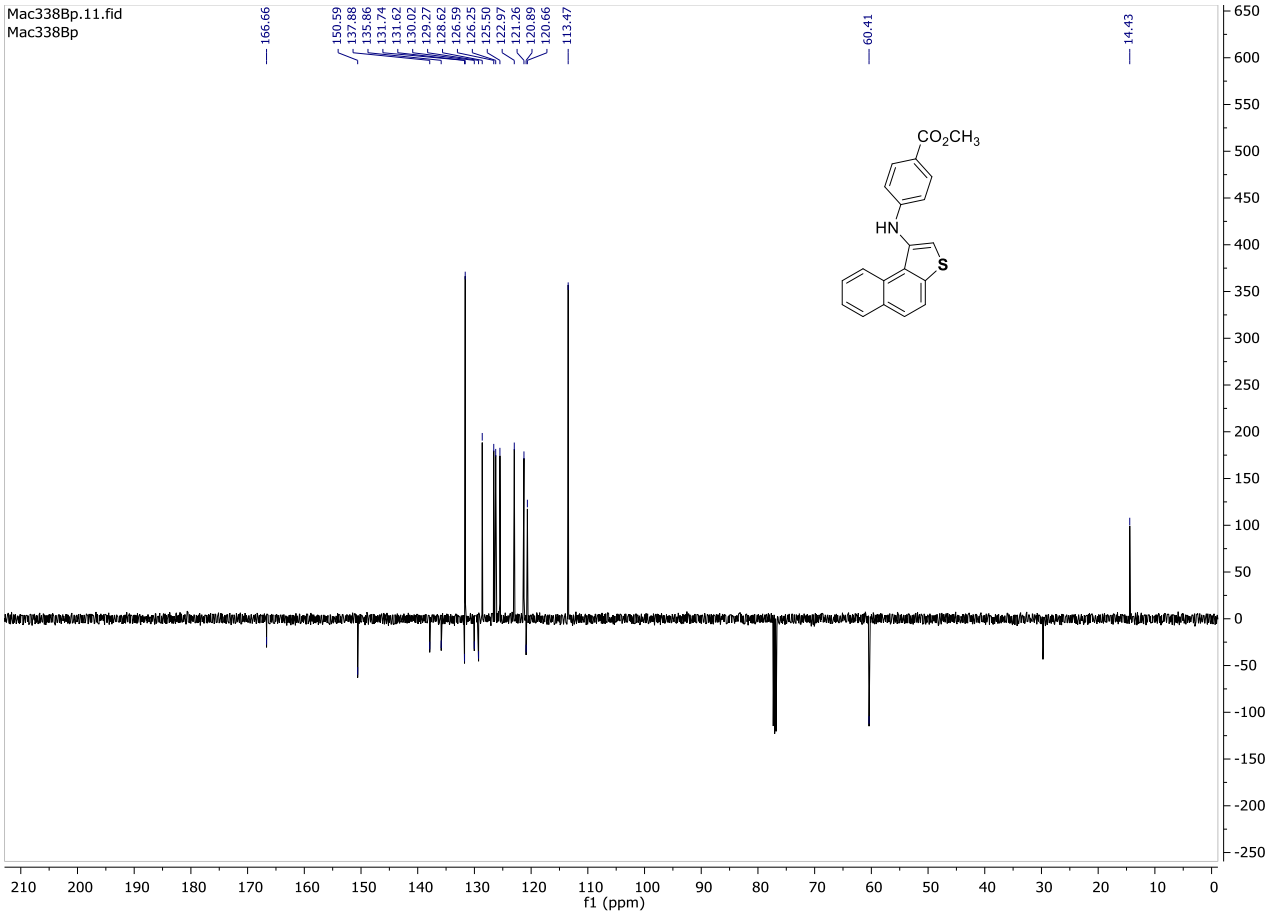
4-(Naphtho[2,1-b]thiophen-1-ylamino)benzonitrile (3an) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)



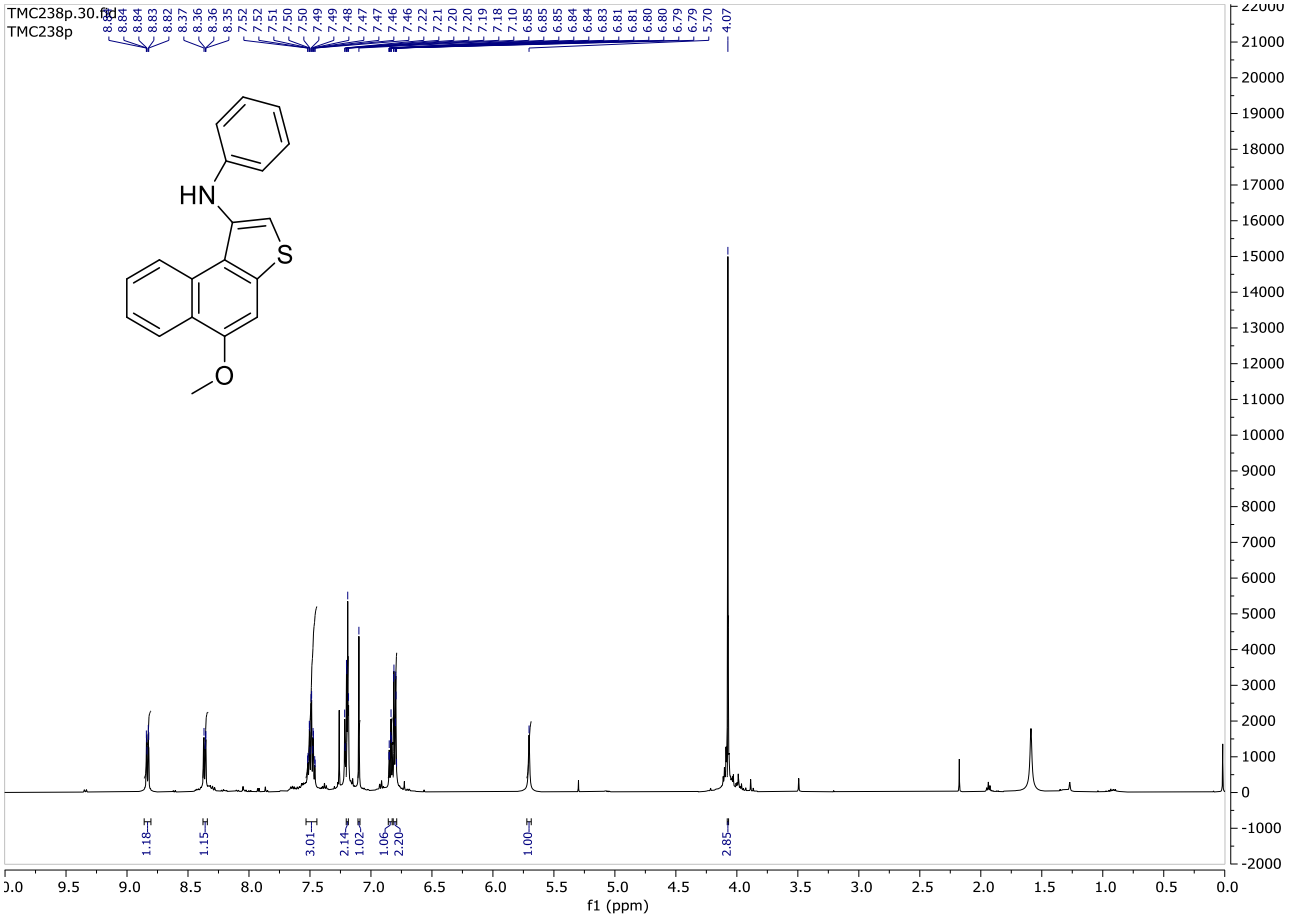


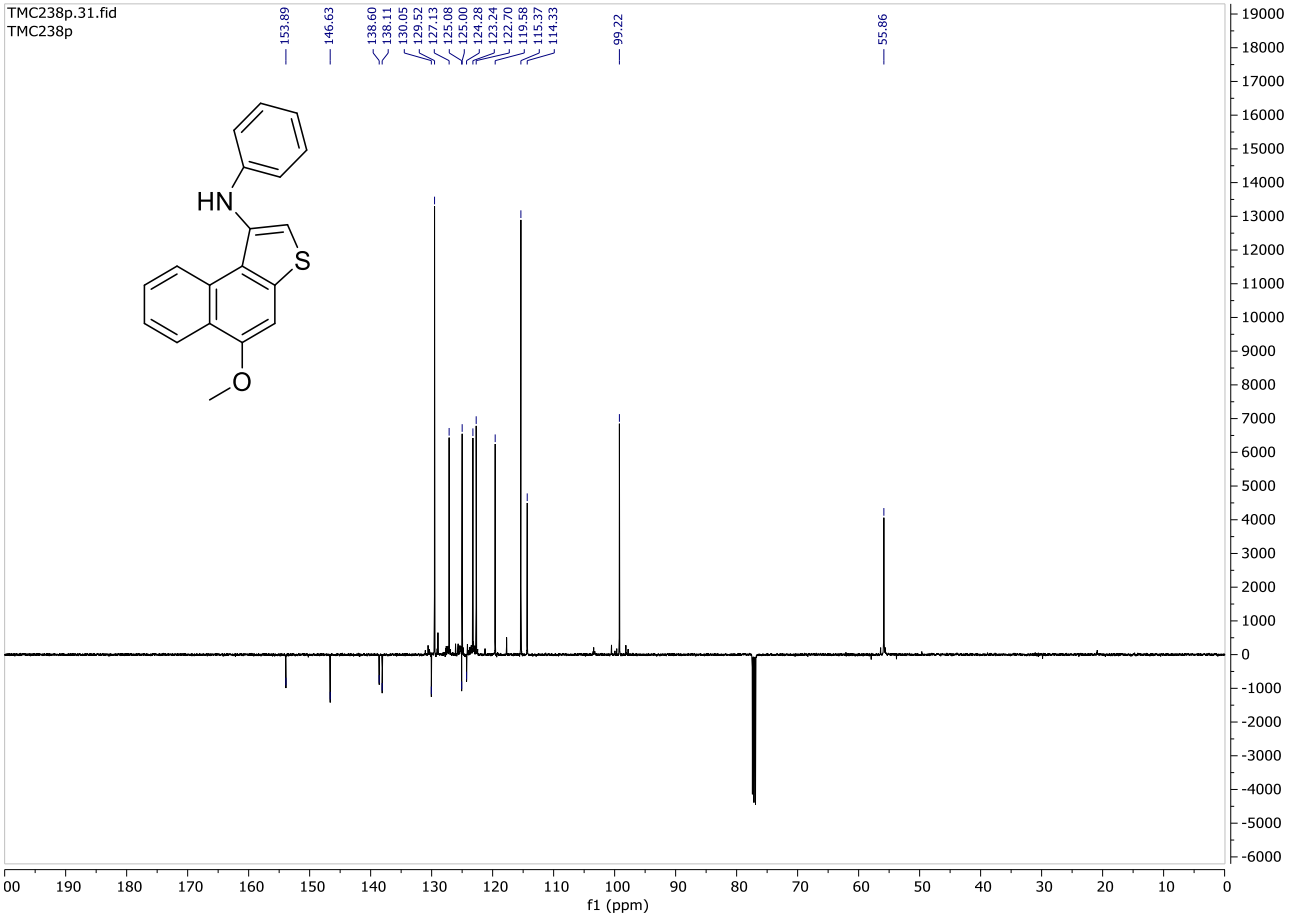
Ethyl 4-(naphtho[2,1-b]thiophen-1-ylamino)benzoate (3ao) (500 MHz and 126 MHz, $CDCl_3$)



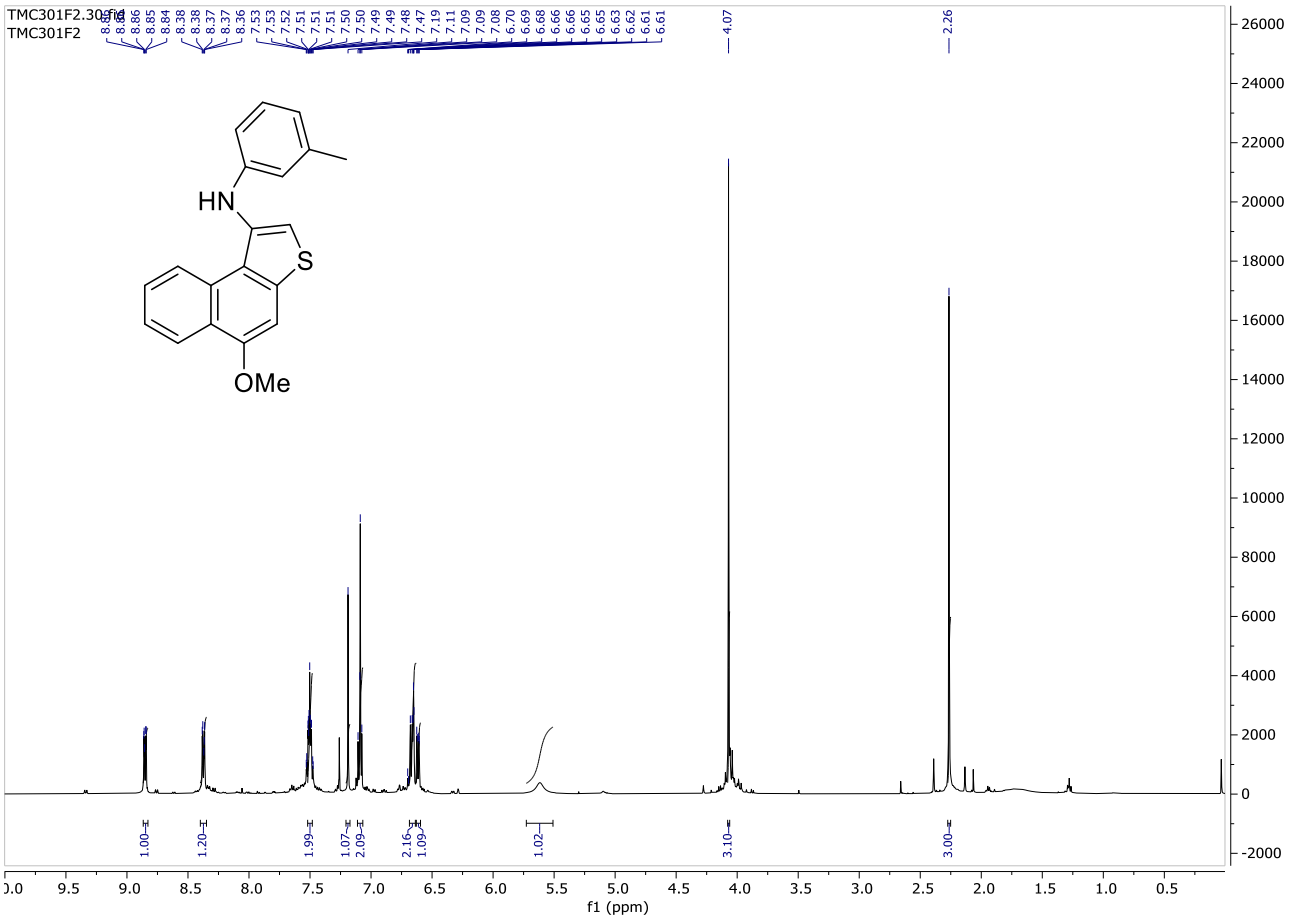


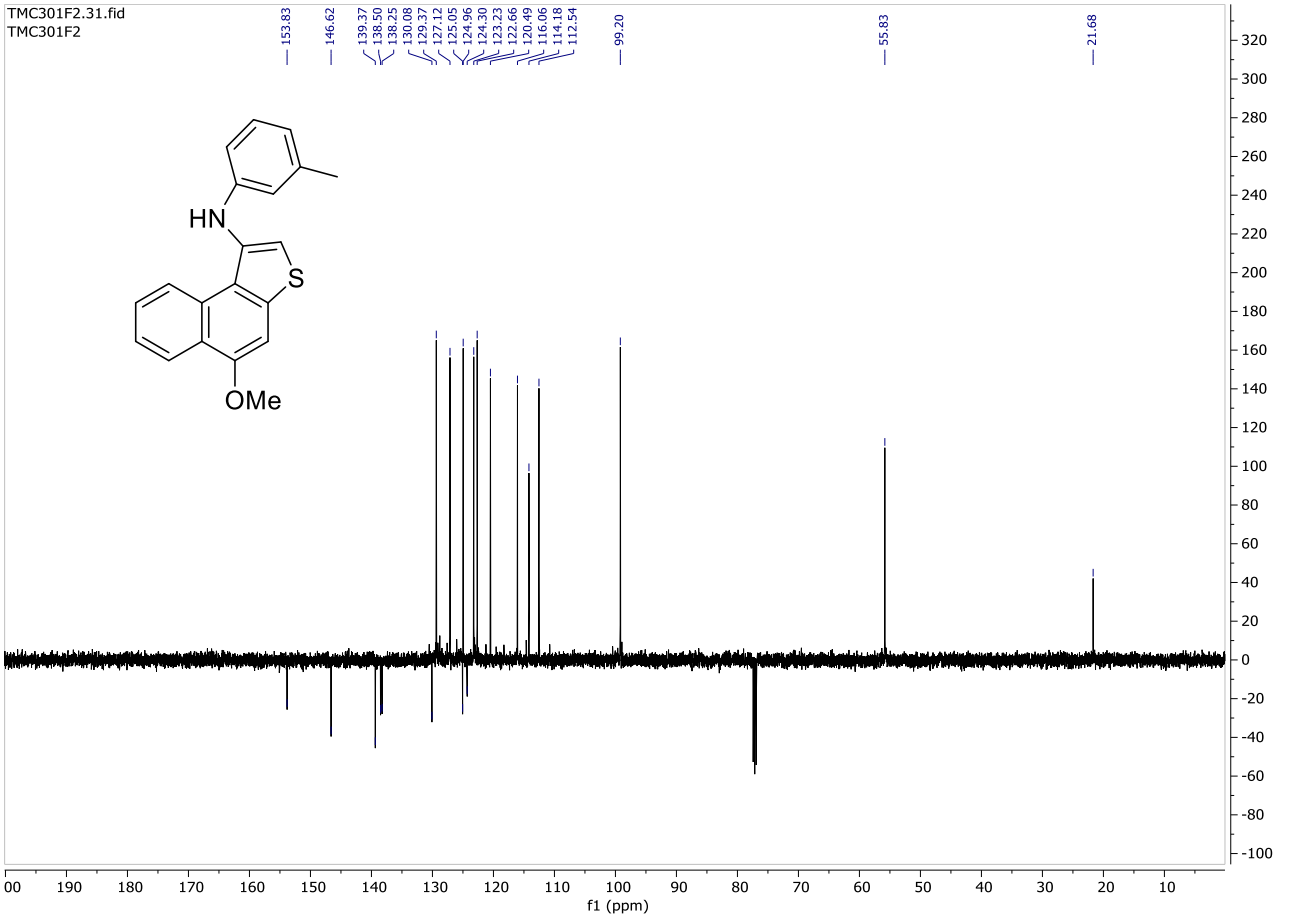
5-Methoxy-*N*-phenylnaphtho[2,1-b]thiophen-1-amine (3ba) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)



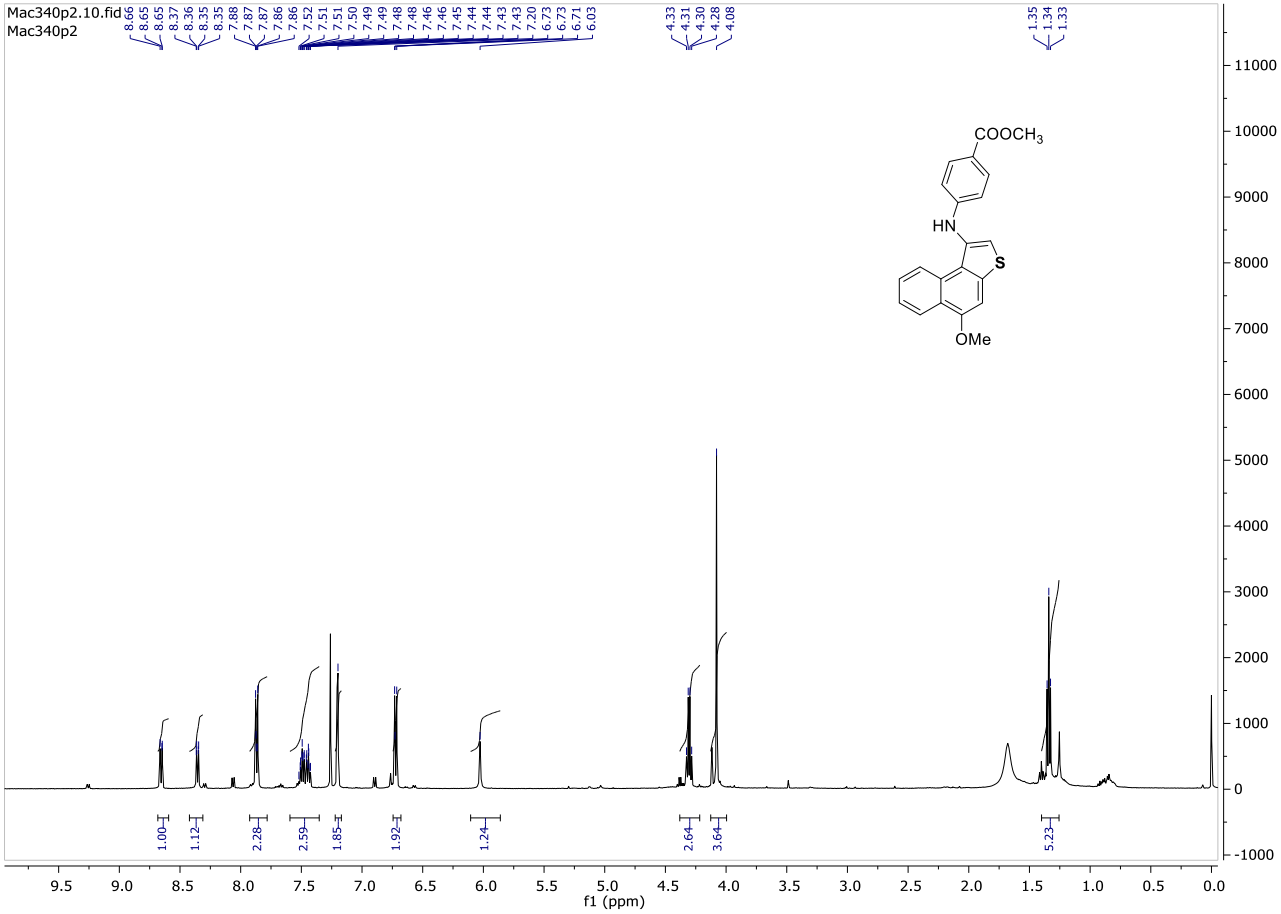


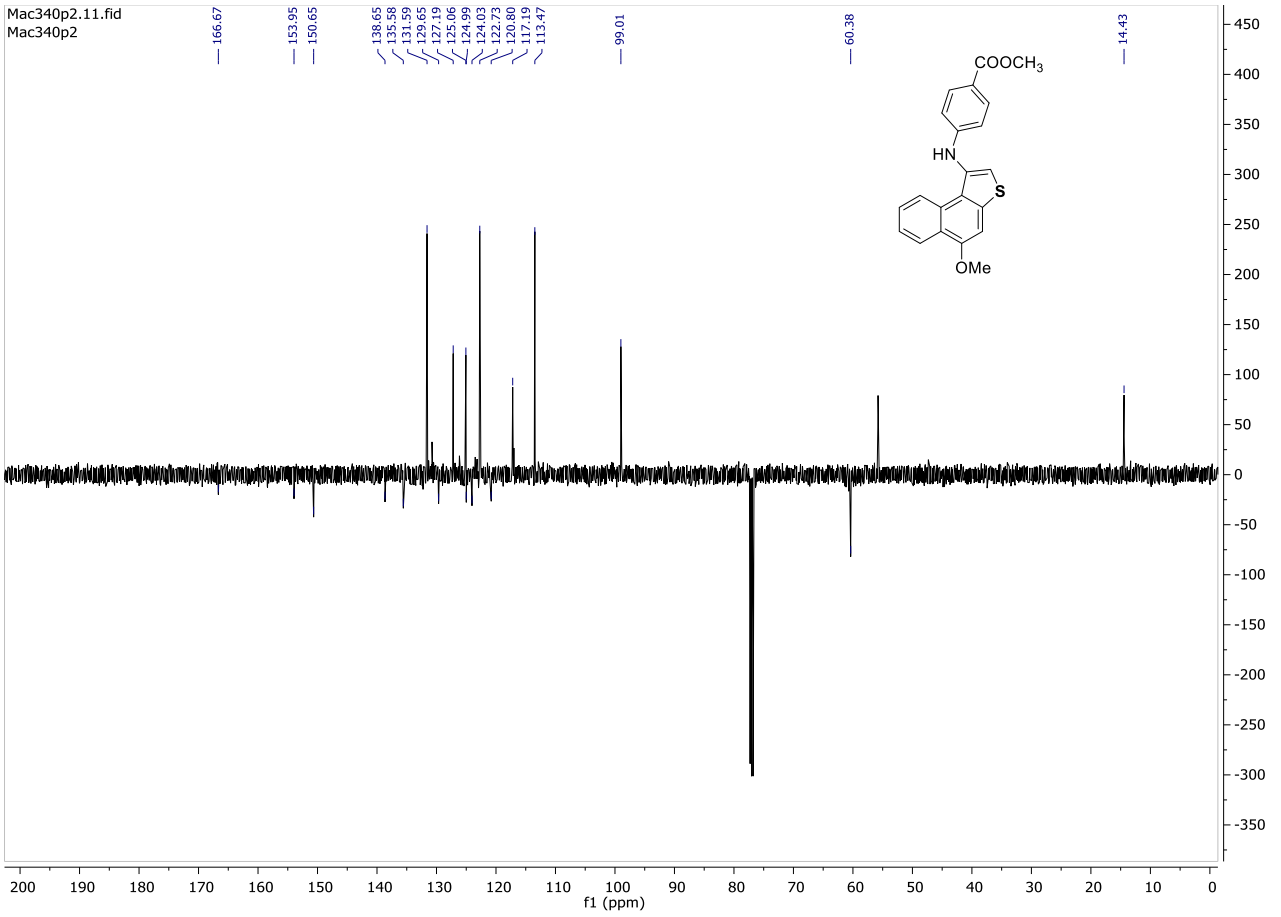
5-Methoxy-*N*-(m-tolyl)naphtho[2,1-b]thiophen-1-amine (3bb) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)





Ethyl 4-((5-methoxynaphtho[2,1-b]thiophen-1-yl)amino)benzoate (3bo) (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz, $CDCl_3$)





1-(*m*-Tolylamino)naphtho[2,1-*b*]thiophene 3,3-dioxide (3ab-O_2)