Supporting Information

DMAP mediated one-pot domino thienannulation: A versatile, regioselective and green mechanochemical route to naphtho[2,3-b]thiophenes

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1. Experimental Section

1.1. General

All reagents were commercial and purchased from Merck, Aldrich, and Fluka and were used as received. \(\beta\)-Oxothioesters and \(\beta\)-Oxothioamides were prepared from literature procedure. \(^1\) \(^1\)H and \(^13\)C NMR spectra were recorded on JEOL AL 300 FT-NMR spectrometer. Chemical shifts are given as \(\delta\) value with reference to tetramethylsilane (TMS) as the internal standard, and coupling constants \((J)\) are given in Hertz. The IR spectra were recorded on Varian 3100 FT-IR spectrophotometer. HRMS data were recorded on Waters-Q-Tof premier HAB 213 spectrometer from IIT Kanpur and Q-Tof micro (YA-105) spectrometer from IIT Bombay using electron spray ionization (ESI) technique. X-ray diffraction analysis was measured on X-calibur Oxford CCD Diffractometer. All the reactions were monitored by TLC using precoated sheets of silica gel G/UV-254 of 0.25 mm thickness (Merck 60F\textsubscript{254}) using UV light for visualization. Melting points were determined with Büchi B-540 melting point apparatus and are uncorrected.

1.2. General procedure

In a mortar \(\alpha\)-enolicdithioester/\(\beta\)-oxothioamides \(1\) (1.0 mmol), 1,4-naphthoquinone \(2\) (0.158 g, 1.0 mmol) and DMAP (0.122 g, 1.0 mmol) was taken and to this 1-2 drops of ethanol was added to make paste. The pasty mixture was ground manually with a mortar and pestle for stipulated period of time (Table 2). After completion of the reaction (monitored by TLC), the whole reaction mixture was dissolved in dichloromethane (20 mL) and washed with water (3 × 15 mL). The organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and subsequently evaporated under reduced pressure. The residue thus obtained was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate-\(n\)-hexane mixture as eluent to afford the desired product \(3\).
1.3. Experimental data of the naphtho[2,3-b]thiophene-4,9-dione derivatives:

3-Benzoyl-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3a):

Red Solid, m.p. 224-226 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.19 (d, $J = 6.9$ Hz, 1H), 8.00 (d, $J = 7.2$ Hz, 1H), 7.85 (d, $J = 7.8$ Hz, 2H), 7.75-7.65 (m, 2H), 7.60-7.56 (m, 1H), 7.47-7.43 (m, 2H), 2.61 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 191.4, 178.2, 176.8, 150.3, 143.7, 141.4, 138.5, 136.4, 134.0, 133.9, 133.8, 133.0, 132.7, 129.2, 128.7, 127.4, 126.8, 20.0; IR (KBr, cm$^{-1}$): 2918, 1670, 1638, 1593, 1245, 720; HRMS [ESI, (M+H)$^+$]: C$_{20}$H$_{13}$O$_3$S$_2$ +, Calcd: 365.0306, Found: 365.0315.

3-(4-Methyl-benzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3b):

Orange Solid, m.p. 225-227 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.20 (d, $J = 6.9$ Hz, 1H), 8.02 (d, $J = 7.2$ Hz, 1H), 7.84 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 7.2$ Hz, 2H), 6.94 (d, $J = 8.7$ Hz, 2H), 3.86 (s, 3H), 2.41 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 191.0, 178.3, 176.9, 150.0, 145.0, 143.7, 141.4, 138.8, 133.9, 133.0, 132.7, 129.5, 129.4, 127.4, 126.8, 21.8, 20.0; IR (KBr, cm$^{-1}$): 2925, 1678, 1643, 1590, 1255, 722.

3-(4-Methoxy-benzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3c):

Red Solid, m.p. 220-222 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.20 (d, $J = 6.9$ Hz, 1H), 8.03 (d, $J = 8.4$ Hz, 1H), 7.84 (d, $J = 8.7$ Hz, 2H), 7.72 (d, $J = 7.2$ Hz, 2H), 6.94 (d, $J = 8.7$ Hz, 2H), 3.86 (s, 3H), 2.61 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 189.9, 178.3, 176.8, 164.2, 149.7, 143.7, 141.2, 138.9, 135.0, 133.9, 133.8, 133.7, 133.0, 132.7, 131.7, 129.4, 128.3, 127.4, 126.8, 55.4, 19.9; IR (KBr, cm$^{-1}$): 2928, 1675, 1643, 1591, 1255, 722; HRMS [ESI, (M+H)$^+$]: C$_{21}$H$_{15}$O$_4$S$_2$ +, Calcd: 395.0411, Found: 395.0429.

3-(4-Bromo-benzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3d):

Orange Solid, m.p. 235-237 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.20 (d, $J = 6.9$ Hz, 1H), 8.03 (d, $J = 8.4$ Hz, 1H), 7.84 (d, $J = 8.7$ Hz, 2H), 7.60 (d, $J = 8.4$ Hz, 2H), 2.63 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 190.4, 178.3, 176.8, 150.9, 141.4, 135.4, 134.0, 133.0, 132.7, 132.1, 130.6, 129.2, 127.5, 126.9, 20.0; IR (KBr, cm$^{-1}$): 2915, 1674, 1632, 1580, 1270, 710; HRMS [ESI, (M + H)$^+$]: C$_{20}$H$_{12}$BrO$_3$S$_2$ +, Calcd: 442.9411, Found: 442.9524.
2-Methylthio-3-(4-trifluoromethyl-benzoyl)-naphtho[2,3-b] thiophene-4,9-dione (3e):

**Red Solid**, m.p. 240-242 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.16 (d, \(J = 7.2\) Hz, 1H), 7.90-7.83 (m, 2H), 7.73-7.65 (m, 2H), 7.58 (d, \(J = 8.1\) Hz, 1H), 7.51-7.46 (m, 1H), 7.39 (d, \(J = 7.5\) Hz, 1H), 2.71 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 189.5, 178.0, 176.9, 142.5, 141.4, 138.4, 137.3, 135.0, 134.4, 134.3, 133.9, 133.7, 130.2, 129.2, 128.4, 127.5, 127.3, 126.8, 126.5, 19.3; IR (KBr, cm\(^{-1}\)): 2925, 1667, 1655, 1592, 1269, 711.

3-(2-Chloro-benzoyl)-2-methylthio-naphtho[2,3-b] thiophene-4,9-dione (3f):

**Red Solid**, m.p. 210-212 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.18 (d, \(J = 7.8\) Hz, 1H), 7.97 (d, \(J = 7.2\) Hz, 1H), 7.69 (s, 3H), 7.41–7.34 (m, 3H), 2.68 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 189.3, 178.1, 176.8, 155.6, 142.8, 141.3, 136.99, 136.95, 134.3, 133.7, 132.94, 132.90, 132.7, 131.3, 130.8, 129.9, 129.5, 127.1, 126.6, 19.4; IR (KBr, cm\(^{-1}\)): 2925, 1668, 1643, 1588, 1265, 723; HRMS [ESI, (M+H)\(^+\)]: C\(_{20}\)H\(_{12}\)ClO\(_3\)S\(_2\)\(^+\), Calcd.: 398.9911, Found: 398.9911.

3-(Benzo[1,3]dioxole-5-carbonyl)-2-methylthio-naphtho[2,3-b] thiophene-4,9-dione (3g):

**Red Solid**, m.p. 218-220 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.19 (s, 1H), 8.03 (s, 1H), 7.81-7.73 (m, 2H), 7.32-7.23 (m, 2H), 6.81 (d, \(J = 8.1\) Hz, 1H), 6.06 (s, 2H), 2.62 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 189.4, 178.3, 176.8, 152.6, 149.7, 148.5, 143.8, 141.3, 138.8, 133.99, 133.93, 133.0, 132.7, 131.4, 127.4, 126.8, 126.6, 108.3, 108.1, 102.0, 20.0; IR (KBr, cm\(^{-1}\)): 2950, 1640, 1620, 1560, 1235, 720; HRMS [ESI, (M+H)\(^+\)]: C\(_{20}\)H\(_{12}\)O\(_2\)S\(_2\)\(^+\), Calcd.: 398.9911, Found: 398.9911.

2-Methylthio-3-(naphthalene-2-carbonyl)-naphtho[2,3-b] thiophene-4,9-dione (3h):

**Red Solid**, m.p. 208-210 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.22 (s, 2H), 8.07 (d, \(J = 8.7\) Hz, 1H), 7.99-7.87 (m, 4H), 7.76-7.57 (m, 3H), 7.53-7.48 (m, 1H), 2.63 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 191.4, 178.3, 176.7, 150.3, 136.0, 134.0, 133.1, 132.8, 132.5, 131.6, 129.6, 128.8, 128.5, 127.8, 127.6, 127.4, 126.8, 124.1, 20.0; IR (KBr, cm\(^{-1}\)): 2952, 1668, 1639, 1592, 1267, 720; HRMS [ESI, (M+H)\(^+\)]: C\(_{24}\)H\(_{15}\)O\(_3\)S\(_2\)\(^+\), Calcd.: 415.0462, Found: 415.0467.
2-Methylthio-3-(pyridine-3-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3i):

**Red Solid**, m.p. 222-224 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.90 (s, 1H), 8.78 (d, \(J = 4.5\) Hz, 1H), 8.26-8.19 (m, 2H), 7.98 (d, \(J = 7.2\) Hz, 1H), 7.77-7.70 (m, 2H), 7.48-7.44 (m, 1H), 2.66 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 190.0, 178.4, 176.7, 153.7, 152.2, 150.6, 143.8, 141.4, 136.5, 136.1, 134.1, 132.9, 132.6, 132.3, 127.4, 126.9, 123.8, 19.9; IR (KBr, cm\(^{-1}\)): 3745, 2924, 1670, 1640, 1582, 1267, 697.

HRMS [ESI, (M+H)+]: C\(_{19}\)H\(_{12}\)NO\(_3\)S\(_2\)^{+}, Calcd.: 366.0253, Found: 366.0256.

2-Methylthio-3-(thiophene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3j):

**Red Solid**, m.p. 205-207 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.22-8.19 (m, 1H), 8.07 (d, \(J = 6.9\) Hz, 1H), 7.75-7.71 (m, 3H), 7.48 (d, \(J = 3.0\) Hz, 1H), 7.12-7.09 (m, 1H), 2.64 (s, 3H); \(^{13}\)C NMR (75MHz, CDCl\(_3\)): \(\delta\) 183.1, 178.2, 176.8, 150.5, 143.8, 143.6, 141.1, 138.1, 135.4, 134.5, 134.0, 133.9, 132.8, 128.3, 127.5, 126.8, 20.0; IR (KBr, cm\(^{-1}\)): 2923, 1674, 1642, 1590, 1269, 712.

HRMS [ESI, (M+H)^+]: C\(_{18}\)H\(_{11}\)O\(_3\)S\(_3\)^{+}, Calcd.: 370.9870, Found: 370.9875.

3-(Furan-2-carbonyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3k):

**Red Solid**, m.p. 215-217 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.21 (d, \(J = 7.5\) Hz, 1H), 8.07 (d, \(J = 6.6\) Hz, 1H), 7.73 (s, 3H), 7.56 (s, 2H), 2.65 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 192.5, 178.4, 178.1, 147.1, 134.2, 134.0, 133.8, 132.9, 127.4, 126.9, 126.3, 119.3, 112.8, 19.8; IR (KBr, cm\(^{-1}\)): 2920, 1670, 1648, 1594, 1270, 710.

3-(2,2-Dimethyl-propionyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3l):

**Red viscous liquid**, \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.11 (d, \(J = 7.5\) Hz, 2H), 7.74 (d, \(J = 5.4\) Hz, 2H), 2.63 (s, 3H), 1.34 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 191.4, 178.3, 176.8, 158.9, 143.6, 134.46, 134.45, 133.0, 132.7, 132.1, 130.6, 128.3, 127.5, 126.9, 43.6, 26.6, 18.0; IR (KBr, cm\(^{-1}\)): 2962, 1650, 1647, 1598, 1258, 714.

3-Benzoyl-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3m):

**Red solid**, m.p. 218-220 °C; \(^1\)H NMR (300 MHz, DMSO): \(\delta\) 9.82 (s, 1H), 8.03 (d, \(J = 7.2\) Hz, 1H), 7.74 (d, \(J = 5.4\) Hz, 2H), 2.63 (s, 3H), 1.34 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 193.1, 179.0, 177.4, 163.5, 141.9, 140.2, 139.0, 133.6, 133.3, 133.2, 132.8, 132.1, 129.9, 129.2, 128.3, 128.2, 127.1, 125.9, 125.6, 120.5, 114.7; IR (KBr, cm\(^{-1}\)): 2926, 1648, 1630, 1590, 1247, 712; HRMS [ESI, (M+H)^+]: C\(_{25}\)H\(_{16}\)NO\(_3\)S^{+}, Calcd.: 410.0851, Found: 410.0859.
Red solid, m.p. 216-218 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.18 (s, 1H), 8.13 (d, $J = 7.5$ Hz, 1H), 7.84 (d, $J = 7.5$ Hz, 1H), 7.71-7.59 (m, 3H), 7.48-7.38 (m, 4H), 7.29-7.19 (m, 4H), 2.41 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 192.7, 179.0, 177.3, 163.0, 143.0, 141.8, 139.0, 137.3, 133.5, 133.3, 133.2, 132.8, 129.8, 129.2, 128.9, 128.6, 127.1, 125.9, 125.4, 120.3, 115.1, 21.6; IR (KBr, cm$^{-1}$): 2925, 1664, 1642, 1595, 1237, 717.

IR (KBr, cm$^{-1}$): 2925, 1662, 1639, 1598, 1247, 709; HRMS [ESI, (M+H)$^+$]: C$_{26}$H$_{18}$NO$_4$S$,^+$ Calcd.: 440.0951, Found: 440.0952.

Red solid, m.p. 230-232 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.98 (s, 1H), 8.15-8.12 (m, 1H), 7.87-7.77 (m, 1H), 7.75-7.60 (m, 1H), 7.46-7.37 (m, 5H), 6.89 (d, $J = 8.7$ Hz, 2H), 3.86 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 199.1, 179.2, 177.1, 150.8, 139.2, 139.1, 133.5, 133.4, 133.0, 132.8, 130.9, 129.8, 129.5, 129.1, 129.0, 128.9, 128.5, 128.0, 127.6, 127.2, 127.1, 55.6; IR (KBr, cm$^{-1}$): 2925, 1662, 1639, 1598, 1247, 719. HRMS [ESI, (M+H)$^+$]: C$_{26}$H$_{18}$NO$_4$S$,^+$ Calcd.: 440.0951, Found: 440.0952.

Red solid, m.p. 206-208 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.16-8.07 (m, 2H), 7.73-7.66 (m, 2H), 5.40 (s, 1H), 3.03 (s, 3H), 1.31 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 211.3, 180.4, 176.1, 163.5, 142.2, 133.8, 133.6, 132.7, 127.2, 126.8, 126.0, 115.2, 46.2, 34.0, 27.4; IR (KBr, cm$^{-1}$): 2962, 1650, 1647, 1598, 1258, 714. HRMS [ESI, (M+H)$^+$]: C$_{18}$H$_{18}$NO$_3$S$,^+$ Calcd.: 328.1002, Found: 328.1007.
3-(3-Methoxy-benzoyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3r):

Red Solid, m.p. 220-222 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.48 (s, 1H), 8.12 (d, $J$ = 7.2 Hz, 2H), 7.78 (d, $J$ = 7.2 Hz, 2H), 7.66-7.58 (m, 2H), 7.02 (d, $J$ = 7.2 Hz, 2H), 3.81 (s, 3H), 3.17 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 192.5, 179.4, 177.0, 170.8, 159.5, 133.7, 133.3, 133.1, 132.9, 129.4, 128.9, 127.0, 125.8, 122.5, 121.1, 120.2, 118.2, 114.3, 112.6, 55.4, 33.9; IR (KBr, cm$^{-1}$): 2928, 1670, 1643, 1596, 1255, 720.

3-(Benzolo[1,3]dioxole-5-carbonyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3s):

Red solid, m.p. 232-234 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.12 (d, $J$ = 7.5 Hz, 2H), 7.84 (d, $J$ = 7.5 Hz, 1H), 7.67-7.60 (m, 2H), 7.17 (d, $J$ = 8.4 Hz, 1H), 6.71 (d, $J$ = 8.1 Hz, 1H), 6.03 (s, 2H), 3.15 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): 191.1, 179.6, 177.0, 170.3, 150.9, 147.9, 143.0, 135.1, 133.7, 133.4, 133.1, 133.0, 128.4, 127.1, 125.9, 124.5, 111.8, 108.4, 107.5, 101.7, 33.9; IR (KBr, cm$^{-1}$): 2927, 1658, 1636, 1594, 1255, 711.

2. References

3. $^1$H and $^{13}$C NMR spectra of Compounds

$^1$H NMR of 3-Benzoyl-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3a)
$^{13}$C NMR of 3-Benzoyl-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3a)
$^1$H NMR of 3-(4-Methylbenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3b)
$^{13}$C NMR of 3-(4-Methylbenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3b)
$^1$H NMR of 3-(4-Methoxybenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3c)
$^{13}$C NMR of 3-(4-Methoxybenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3c)
$^1$H NMR of 3-(4-Bromobenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3d)
$^{13}$C NMR of 3-(4-Bromobenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3d)
$^1$H NMR of 2-Methylthio-3-(4-trifluoromethylbenzoyl)-naph[2,3-b]thiophene-4,9-dione (3e)
$^{13}$C NMR of 2-Methylthio-3-(4-trifluoromethylbenzoyl)-naphtho[2,3-b]thiophene-4,9-dione (3e)
$^1$H NMR of 3-(2-Chlorobenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3f)
$^{13}$C NMR of 3-(2-Chlorobenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3f)
$^1$H NMR of 3-(Benzo[1,3]dioxole-5-carbonyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3g)
$^{13}C$ NMR of 3-(Benzo[1,3]dioxole-5-carbonyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3g)
$^1$H NMR of 2-Methylthio-3-(naphthalene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3h)
$^{13}$C NMR of 2-Methylthio-3-(naphthalene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3h)
$^1$H NMR of 2-Methylthio-3-(pyridine-3-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3i)
$^{13}$C NMR of 2-Methylthio-3-(pyridine-3-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3i)
$^1$H NMR of 2-Methylthio-3-(thiophene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3j)
$^{13}$C NMR of 2-Methylthio-3-(thiophene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3j)
\textsuperscript{1}H NMR of 3-(Furan-2-carbonyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3k)
$^{13}$C NMR of 3-(Furan-2-carbonyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3k)
$^{13}C$ NMR of 3-(2,2-Dimethylpropionyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3l)
$^1$H NMR of 3-Benzoyl-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3m)
$^{13}$C NMR of 3-Benzoyl-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3m)
$^1$H NMR of 3-(4-Methyl-benzoyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3n)
$^{13}$C NMR of 3-(4-Methyl-benzoyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3n)
$^1$H NMR of 3-(4-Methoxy-benzoxyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3o)
$^{13}$C NMR of 3-(4-Methoxy-benzoyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3o)
$^1\text{H NMR of 3-(Biphenyl-4-carbonyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3p)}$
$^{13}$C NMR of 3-(Biphenyl-4-carbonyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3p)
$^1$H NMR of 3-(2,2-Dimethyl-propionyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3q)
$^{13}$C NMR of 3-(2,2-Dimethyl-propionyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3g)
$^1$H NMR of 3-(3-Methoxy-benzoyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3r)
$^{13}$C NMR of 3-(3-Methoxy-benzoyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3r)
$^1H$ NMR of 3-(Benzo[1,3]dioxole-5-carbonyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3s)
$^{13}$C NMR of 3-(Benzo[1,3]dioxole-5-carbonyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3s)
4. HRMS data of some selected compounds

**HRMS data of 3-Benzoyl-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3a)**

Electronic Supplementary Material (ESI) for RSC Advances
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HRMS data of 3-(4-Methoxybenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3c)
HRMS data of 3-(4-Bromobenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3d)
HRMS data of 3-(2-Chloro-benzoyl)-2-methylthio-naphtho[2,3-b] thiophene-4,9-dione (3f)

[Graph showing mass spectrum with molecular ion at 368.9511 and various fragment ions indicated by m/z values.]
HRMS data of 2-Methylthio-3-(naphthalene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3h)
HRMS data of 2-Methylthio-3-(pyridine-3-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3i)
HRMS data of 2-Methylthio-3-(thiophene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3j)
HRMS data of 3-Benzoyl-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3m)
HRMS data of 3-(4-Methoxy-benzoyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3o)
HRMS data of 3-(Biphenyl-4-carbonyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3p)
HRMS data of 3-(2,2-Dimethyl-propionyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3q)
5. Crystallography data of 3f, 3j and 3q

Crystal data for 3f: C_{20}H_{11}ClO_{3}S_{2}, Red, M = 397.98, Monoclinic, space group P 1 21/n 1, a = 9.1727(12), b = 12.4922(14), c = 15.7956 (17) Å, V = 1749.4(3) Å³, μ = 0.475 mm⁻¹, Z = 4, T = 293 K, F_{000} = 816, R = 0.0636, wR² = 0.1954. The CCDC deposition number: CCDC 881391.

Crystal data for 3j: C_{18}H_{10}O_{3}S_{3}, Red, M = 370.46, Triclinic, space group P-1, a = 8.245(5), b = 8.504(5), c = 12.515(5) Å, V = 795.2(7) Å³, μ = 0.480 mm⁻¹, Z = 2, T = 293 K, F_{000} = 380, R = 0.0439, wR² = 0.1285. The CCDC deposition number: CCDC 881392.

Crystal data for 3q: C_{18}H_{17}NO_{3}S, Red, M = 327.40, Triclinic, space group P -1, a = 6.1217(14), b = 11.429(3), c = 11.589(3) Å, V = 793.3(3) Å³, μ = 0.219 mm⁻¹, Z = 2, T = 293 K, F_{000} = 344, R = 0.1058, wR² = 0.3071. The CCDC deposition number: CCDC 915292.