Supplementary data

**Cu-catalyzed in situ** generation of thiol using xanthate as thiol surrogate for the one-pot synthesis of benzothiazoles and benzothiophenes

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General considerations

Cu(OAc)₂.H₂O was purchased from Merck, India and oven dried to obtain anhydrous Cu(OAc)₂. Aryl halides, acid chlorides, alkynes and potassium ethyl xanthogenate were purchased from sigma Aldrich Chemical Company. All the solvents used for the reactions were obtained from Rankem, India and dried by Vogel’s procedure. Reaction temperatures were controlled by Varivolt temperature modulator, Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F₂₅₄ precoated plates (0.25 mm) and visualized by UV fluorescence quenching. Silica gel (particle size 100-200 mesh) purchased from SRL India was used for chromatography. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz instrument. ¹H NMR spectra were reported relative to Me₄Si (δ 0.0 ppm) or residual CHCl₃ (δ 7.26 ppm). ¹³C NMR were reported relative to CDCl₃ (δ 77.16 ppm). FTIR spectra were recorded on a Nicolet 6700 spectrometer and are reported in frequency of absorption (cm⁻¹). High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer.

Typical experimental procedure for synthesis of 2-idoanilides

To a solution of o-iodoaniline (2 mmol) in dry THF (10 mL), acid chloride (2.4 mmol) was added and the resulting mixture was stirred at room temperature for 12 hours.¹ Then, ethyl acetate was added and the organic layer was washed twice with saturated NaHCO₃, once with brine, twice with HCl (2N aqueous solution), then dried over anhydrous Na₂SO₄ and concentrated. The crude residue was purified by column chromatography.

N-(2-Iodophenyl)benzamide (2)¹

White solid; mp 132-133 °C (lit. 133–134 °C); Rf 0.44 (1:9 ethyl acetate : hexanes); ¹H NMR (400 MHz, CDCl₃): δ 6.86-6.93 (m, 1H), 7.38-7.45 (m, 1H), 7.50-7.63 (m, 3H), 7.82 (dd, J = 0.4 & 7.8 Hz, 1H), 7.95-8.00 (m, 2H), 8.30 (bs, 1H), 8.46 (dd, J = 0.8 & 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 90.5, 116.1, 116.3, 122.0, 126.3, 129.6, 129.7, 129.8, 138.2, 139.0, 164.4; FTIR (neat): 3400, 1668, 1035 cm⁻¹; HRMS: m/z [M+H]⁺ calcd for C₁₃H₁₁NOI: 323.9885; found: 323.9884.
N-(2-Iodophenyl)-4-methoxybenzamide (4)²

White solid; mp 150–153 °C (lit. 151–152 °C); Rf 0.32 (1:9 ethyl acetate : hexanes); ¹H NMR (400 MHz, CDCl₃): δ 3.88 (s, 3H), 6.81-6.89 (m, 1H), 6.97-7.05 (m, 2H), 7.35-7.41 (m, 1H), 7.80 (dd, J = 1.6 & 7.8 Hz, 1H), 7.91-7.96 (m, 2H), 8.20 (bs, 1H), 8.44 (dd, J = 1.6 & 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 55.7, 90.3, 114.4, 121.9, 125.9, 127.1, 129.3, 129.6, 138.8, 138.9, 163.0, 165.0; FTIR (neat): 3281, 1649, 1026, 843, 759 cm⁻¹; HRMS: m/z [M+Na]+ calcd for C₁₄H₁₂NO₂NaI: 375.9811, found: 375.9813.

N-(2-Iodophenyl)-3-methoxybenzamide (6)³

White solid; mp 95 °C (lit. 94–95.5 °C); Rf 0.33 (1:9 ethyl acetate : hexanes); ¹H NMR (400 MHz, CDCl₃): δ 3.9 (s, 3H), 6.86–6.93 (m, 1H), 7.10–7.15 (m, 1H), 7.38–7.47 (m, 2H), 7.49–7.55 (m, 2H), 7.83 (dd, J = 1.6 & 8.0 Hz, 1H), 8.29 (bs, 1H), 8.46 (dd, J = 1.2 & 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 55.7, 90.3, 112.7, 118.6, 119.0, 121.9, 126.2, 129.5 130.1, 136.2, 138.4, 139.0, 160.2, 165.3; FTIR (neat): 3400, 1668, 1035, 750 cm⁻¹; HRMS: m/z [M+Na]+ calcd for C₁₄H₁₂NO₂NaI: 375.9810; found: 359.9806.

N-(2-Iodophenyl)-2-methylbenzamide (8)⁴

White solid; mp 100-101 °C (Lit. 101-102 °C); Rf 0.48 (1:9 ethyl acetate : hexanes); ¹H NMR (400 MHz, CDCl₃): δ 2.6 (s, 3H), 6.89 (td, J = 1.2 & 7.6, 1H), 7.25-7.36 (m, 2H), 7.38-7.45 (m, 2H), 7.58–7.65 (m, 1H), 7.82 (dd, J = 1.2 & 8.0 Hz, 2H), 8.38–8.46 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 20.3, 90.4, 122.2, 126.2, 126.3, 126.9, 129.5, 130.8, 131.7, 136.0, 137.1, 138.6, 139.0, 168.0; FTIR (neat): 3260, 1654, 1047, 752, 672 cm⁻¹; HRMS: m/z [M+Na]+ calcd for C₁₄H₁₂NONaI: 359.9861; found: 359.9863.

4-Fluoro-N-(2-iodophenyl)benzamide (10)⁵

White solid; mp 113–115 °C (lit. 114–118 °C); Rf 0.44 (1:9 ethyl acetate : hexanes); ¹H NMR (400 MHz, CDCl₃): δ 6.89 (td, J = 1.2 & 7.6 Hz, 1H), 7.10-7.27 (m, 2H), 7.37-7.44 (m, 1H), 7.82 (dd, J
=1.2 & 8.0 Hz, 1H), 7.94-8.03 (m, 2H), 8.22 (bs, 1H), 8.41 (dd, J =1.2 & 8.2 Hz, 1H);

\[ ^{13} \text{C NMR (100 MHz, CDCl}_3 \]: \delta 90.5, 116.2 (d, J = 22.0 Hz), 121.9, 126.3, 129.6 (d, J = 8.6 Hz), 129.8, 130.9, 138.2, 139.0, 164.4, 165.3 (d, J = 249.6 Hz); FTIR (neat): 3275, 1648, 1020, 758 cm\(^{-1}\); HRMS: m/z [M+Na\(^+\) calcd for C\(_{13}\)H\(_9\)NONaFI: 363.9611, found: 363.9616.

N-(2-Iodo-4-methylphenyl)benzamide (12)

White solid; mp 160-162 °C; R\(_f\) 0.31 (1:19 ethyl acetate : hexanes);
\[ ^1 \text{H NMR (400 MHz, CDCl}_3 \]: \delta 2.31 (s, 3H), 7.21 (d, J = 7.6 Hz, 1H), 7.49-7.61 (m, 3H), 7.65 (d, J = 0.8 Hz, 1H), 7.94-7.99 (m, 2H), 8.21 (bs, 1H), 8.29 (d, J = 8.4 Hz, 1H); \[ ^{13} \text{C NMR (100 MHz, CDCl}_3 \]: \delta 20.5, 90.5, 121.7, 127.3, 129.1, 130.2, 132.2, 134.8, 135.9, 136.2, 139.1, 165.4; IR (neat): 3252, 3055, 3000, 1648, 818, 711 cm\(^{-1}\); HRMS (m/z): [M+Na\(^+\) calcd. for C\(_{14}\)H\(_{12}\)NONaI: 359.9861; found: 359.9875.

N-(2-Iodophenyl)pivalamide (14)

White solid; mp 68-69 °C (lit. 67-69 °C); R\(_f\) 0.70 (1:9 ethyl acetate : hexanes);
\[ ^1 \text{H NMR (400 MHz, CDCl}_3 \]: \delta 1.29 (s, 9H), 6.70-6.82 (m, 1H), 7.22-7.31 (m, 1H), 7.64-7.83 (m, 1H), 8.21 (d, J = 8.4 Hz, 1H);

\[ ^{13} \text{C NMR (100 MHz, CDCl}_3 \]: \delta 29.0, 41.0, 92.0, 123.0, 127.0, 130.0, 139.0, 139.5, 174.0; FTIR (neat): 2932, 1556, 1170, 735 cm\(^{-1}\).

N-(2-Iodophenyl)propionamide (16)

White solid; mp 94-95 °C; R\(_f\) 0.37 (1:9 ethyl acetate : hexanes);
\[ ^1 \text{H NMR (400 MHz, CDCl}_3 \]: \delta 1.29 (t, J = 7.6 Hz, 3H), 2.47 (q, J = 7.6 Hz, 2H), 6.80-6.87 (m, 1H), 7.31-7.37 (m, 1H), 7.46 (bs, 1H), 7.77 (dd, J = 8.0 & 1.2 Hz, 1H), 8.24 (d, J = 7.6 Hz, 1H); \[ ^{13} \text{C NMR (100 MHz, CDCl}_3 \]: \delta 9.8, 31.2, 90.1, 122.1, 125.9, 129.4, 138.3, 138.9, 172.1; IR (neat): 3276, 3025, 2969, 2934,
2873, 1656, 760, 671 cm\(^{-1}\); HRMS (m/z): [M+H]\(^{+}\) calcd. for C\(_{9}\)H\(_{11}\)NOI: 275.9885; found: 275.9893.

\(N\)-(4-benzoyl-2-iodophenyl)benzamide (18)

White solid; mp 162-163 °C; R\(_{f}\) 0.36 (1:9 ethyl acetate : hexanes); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.48-7.66 (m, 6H), 7.76-7.81 (m, 2H), 7.83 (d, \(J = 8.4\) Hz, 1H), 7.97-8.03 (m, 2H), 8.36 (d, \(J = 1.6\) Hz, 1H), 8.56 (bs, 1H), 8.65 (d, \(J = 8.4\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 89.5, 120.0, 127.4, 128.6, 129.2, 130.0, 130.3, 132.0, 132.8, 134.2, 134.6, 137.4, 140.7, 141.9, 165.5, 194.2; IR (neat): 3286, 3059, 1659, 1650, 799, 724, 701 cm\(^{-1}\); HRMS (m/z): [M+H]\(^{+}\) calcd. for C\(_{20}\)H\(_{15}\)NO\(_2\)I: 428.0148; found: 428.0136.

Methyl 4-benzamido-3-iodobenzoate (20)

White solid; mp 146-147 °C (lit. 144-146 °C); R\(_{f}\) 0.40 (1:9 ethyl acetate : hexanes); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 3.92 (s, 3H), 7.50-7.65 (m, 3H), 7.95-8.01 (m, 2H), 8.07 (dd, \(J = 8.8\) & 1.6 Hz, 1H), 8.50 (d, \(J = 2.0\) Hz, 1H), 8.52 (bs, 1H), 8.63 (d, \(J = 8.8\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 52.5, 88.9, 120.2, 127.2, 127.4, 129.2, 131.2, 132.7, 134.3, 140.4, 142.3, 165.4, 165.5; IR (neat): 3378, 2957, 2923, 2853, 1710, 1683, 763, 699 cm\(^{-1}\); HRMS (m/z): [M+H]\(^{+}\) calcd. for C\(_{15}\)H\(_{13}\)NO\(_3\)I: 381.9940; found: 381.9945.

\(N\)-(5-Fluoro-2-iodophenyl)-3,4-dimethoxybenzamide (24)

White solid; mp 166-168 °C; R\(_{f}\) 0.27 (1:4 ethyl acetate : hexanes); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 3.96 (s, 3H), 3.97 (s, 3H), 6.62-6.69 (m, 1H), 6.96 (d, \(J = 8.0\) Hz, 1H), 7.51 (dd, \(J = 8.4\) & 2.4 Hz, 1H), 7.54 (d, \(J = 2.0\) Hz, 1H), 7.73 (dd, \(J = 8.4\) & 6.0 Hz, 1H), 8.30 (bs, 1H), 8.37 (dd, \(J = 11.2\) & 2.8 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 56.19, 56.24, 82.4, 108.9 (d, \(J = 28.6\) Hz), 110.7, 110.8, 113.0 (d, \(J = 22.5\) Hz), 119.9, 126.8, 139.2 (d, \(J = 8.9\) Hz), 139.8 (d, \(J = 11.8\) Hz), 149.5, 152.7, 163.5 (d, \(J = 224.8\) Hz), 164.9; IR
(neat): 3385, 3061, 3011, 2931, 2837, 1665, 745 cm\(^{-1}\); HRMS \((m/z)\): [M+H]\(^+\) calcd. for C\(_{15}\)H\(_{14}\)NO\(_{3}\)FI: 402.0002; found: 402.0004.

Typical experimental procedure for synthesis of \(o\)-haloalkynylbenzenes

A solution of Et\(_3\)N (12.5 mL), PdCl\(_2\)(PPh\(_3\))\(_2\) (2 mol%), CuI (1 mol%), 1,2-dihalobenzene (5 mmol) and terminal alkyne (6 mmol) was stirred for 5 minutes before flushing with N\(_2\) and then the round bottom flask was closed.\(^8\) The reaction mixture was allowed to stir at room temperature for 8-12 hours and the resulting solution was filtered and washed with saturated aq. NaCl solution and extracted with ethyl acetate (2 x 15 mL). The combined organic fractions were dried over anhydrous Na\(_2\)SO\(_4\) and then the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexanes as eluents.

1-Iodo-2-(phenylethynyl)benzene (31)\(^8\)

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{I} \\
\end{array}
\]

Pale yellow oil; \(R_f\) 0.64 (in hexanes); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.99-7.05 (m, 1H), 7.31-7.40 (m, 4H), 7.52-7.56 (m, 1H), 7.59-7.64 (m, 2H), 7.89 (d, \(J = 8.0\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 91.8, 93.2, 101.3, 123.0, 127.9, 128.5, 128.8, 129.5, 129.9, 131.8, 132.6, 138.9; IR (neat): 3057, 2955, 2924, 2218, 753, 689 cm\(^{-1}\); HRMS \((m/z)\): [M+H]\(^+\) calcd. for C\(_{14}\)H\(_{10}\)I: 304.9827; found: 304.9820.

1-Iodo-2-(\(p\)-tolylethynyl)benzene (33)\(^9\)

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{I} \\
\end{array}
\]

White solid; mp 89-90 °C (lit. 88-90 °C); \(R_f\) 0.60 (in hexanes); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 2.38 (s, 3H), 6.96-7.04 (m, 1H), 7.18 (d, \(J = 7.6\) Hz, 2H), 7.33 (t, \(J = 7.6\) Hz, 1H), 7.47-7.57 (m, 3H), 7.88 (d, \(J = 8.0\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 21.7, 91.2, 93.5, 101.3, 119.9, 127.9, 129.3, 130.1, 131.7, 132.4, 132.5, 138.8, 139.0; IR (neat): 3050, 2916, 2854, 2213, 814, 755 cm\(^{-1}\); HRMS \((m/z)\): [M+H]\(^+\) calcd. for C\(_{15}\)H\(_{12}\)I: 318.9984; found: 318.9972.
1-Iodo-2-((m-tolylethynyl)benzene (35)

Colorless liquid; R\textsubscript{f} 0.70 (in hexanes); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 2.29 (s, 3H), 6.89-6.96 (m, 1H), 7.10 (d, \(J = 7.6\) Hz, 1H), 7.14-7.29 (m, 2H), 7.30-7.36 (m, 2H), 7.42-7.47 (m, 1H), 7.80 (d, \(J = 8.0\) Hz, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 21.4, 91.4, 93.4, 101.3, 122.9, 127.9, 128.4, 128.9, 129.4, 129.7, 130.0, 132.3, 132.5, 138.2, 138.9; IR (neat): 3052, 2921, 2857, 2208, 784, 751, 689 cm\textsuperscript{-1}; HRMS (m/z): [M+K]\textsuperscript{+} calcd. for C\textsubscript{15}H\textsubscript{11}KI: 356.9543; found: 356.9543.

1-((2-Iodophenyl)ethynyl)-4-methoxy-2-methylbenzene (37)

White solid; mp 50-52 °C; R\textsubscript{f} 0.38 (in hexanes); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 2.58 (s, 3H), 3.82 (s, 3H), 6.74 (dd, \(J = 8.4\) & 2.8 Hz, 1H), 6.79 (d, \(J = 2.4\) Hz, 1H), 6.99 (td, \(J = 7.6\) & 1.6 Hz, 1H), 7.32 (td, \(J = 7.6\) & 0.8 Hz, 1H), 7.48-7.56 (m, 2H), 7.85-7.90 (m, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 21.7, 55.4, 92.5, 94.0, 100.6, 111.5, 115.1, 115.3, 127.9, 129.0, 130.6, 132.6, 133.7, 138.8, 142.6, 160.0; IR (neat): 3053, 3006, 2962, 2921, 2840, 2203, 811, 749 cm\textsuperscript{-1}; HRMS (m/z): [M+H]\textsuperscript{+} calcd. for C\textsubscript{16}H\textsubscript{14}OI: 349.0089; found: 349.0091.

1-((4-Fluorophenyl)ethynyl)-2-iodobenzene (39)

White solid; mp 55-56 °C; R\textsubscript{f} 0.70 (in hexanes); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 6.97-7.15 (m, 3H), 7.33 (t, \(J = 7.2\) Hz, 1H), 7.52 (d, \(J = 7.2\) Hz, 1H), 7.55-7.66 (m, 2H), 7.88 (d, \(J = 7.6\) Hz, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 91.5, 92.1, 101.2, 115.9 (d, \(J = 22.0\) Hz), 119.2, 127.9, 129.6, 129.8, 132.5, 133.7 (d, \(J = 8.3\) Hz), 138.9, 162.9 (d, \(J = 248.6\) Hz); IR (neat): 3054, 2985, 2221, 838, 798, 740, 706 cm\textsuperscript{-1}; HRMS (m/z): [M+H]\textsuperscript{+} calcd. for C\textsubscript{14}H\textsubscript{9}IF: 322.9733; found: 322.9747.

1-(Cyclohexenylethynyl)-2-iodobenzene (41)

Colorless liquid; R\textsubscript{f} 0.72 (in hexanes); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 1.59-1.74 (m, 4H), 2.12-2.20 (m, 2H), 2.25-2.32 (m, 2H), 6.28-
6.33 (m, 1H), 6.95 (td, $J = 8.0 \& 1.6$ Hz, 1H), 7.27 (td, $J = 8.0 \& 0.8$ Hz, 1H), 7.42 (dd, $J = 7.6 \& 1.6$ Hz, 1H), 7.81-7.85 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 21.6, 22.4, 26.0, 29.0, 89.4, 95.2, 101.3, 120.8, 127.9, 128.9, 130.4, 132.3, 136.2, 138.7; IR (neat): 2985, 2940, 2204, 2086, 848, 787, 758 cm$^{-1}$; HRMS ($m/z$): [M+K]$^+$ calcd. for C$_{14}$H$_{13}$KI: 346.9699; found: 346.9695.

2-((2-Iodophenyl)ethynyl)pyridine (43)$^{10}$

Yellow color liquid; R$_f$ 0.31 (1:9 ethyl acetate : hexanes); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.99 (td, $J = 8.0 \& 1.6$ Hz, 1H), 7.17-7.23 (m, 1H), 7.28 (t, $J = 7.6$ Hz, 1H), 7.52-7.58 (m, 2H), 7.64 (td, $J = 8.0 \& 1.6$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 8.58 (d, $J = 4.8$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 91.2, 92.0, 101.3, 123.2, 127.7, 128.0, 129.0, 130.2, 133.3, 136.3, 138.9, 143.3, 150.3; IR (neat): 2925, 2941, 2225, 2087, 848, 783, 761 cm$^{-1}$.

1-Bromo-2-(phenylethynyl)benzene (45)$^{11}$

Pale yellow oil; R$_f$ 0.62 (in hexanes); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.18 (td, $J = 7.6 \& 2.0$ Hz, 1H), 7.30 (td, $J = 7.6 \& 1.2$ Hz, 1H), 7.34-7.39 (m, 3H), 7.54-7.64 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 88.1, 94.1, 123.0, 125.5, 125.8, 127.2, 128.5, 128.8, 129.5, 131.8, 132.6, 133.4; IR (neat): 3063, 2984, 2223, 760, 692 cm$^{-1}$.

1-Bromo-2-(p-tolylethynyl)benzene (46)$^{11}$

Pale yellow solid; mp 85-86 °C (lit. 86-87 °C); R$_f$ 0.66 (in hexanes); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.42 (s, 3H), 7.16-7.42 (m, 4H), 7.49-7.72 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 21.7, 87.6, 94.3, 119.9, 125.7, 127.1, 129.3, 129.7, 131.7, 132.5, 133.3, 139.0, 139.6; IR (neat): 3056, 3025, 2918, 2853, 2214, 812, 750 cm$^{-1}$; HRMS ($m/z$): [M+H]$^+$ calcd. for C$_{15}$H$_{12}$Br: 271.0122; found: 271.0121.
2-((2-Bromophenyl)ethynyl)pyridine (47)

Yellow color liquid; Rf 0.30 (1:9 ethyl acetate : hexanes); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.12-7.21 (m, 2H), 7.24 (td, J = 7.6 & 1.2 Hz, 1H), 7.50-7.58 (m, 3H), 7.62 (td, J = 8.0 & 2.0 Hz, 1H), 8.55-8.59 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 87.7, 92.9, 123.2, 124.6, 126.0, 127.2, 127.7, 130.2, 132.6, 133.9, 136.3, 143.3, 150.3; IR (neat): 3053, 2983, 2253, 743, 651 cm$^{-1}$; HRMS (m/z): [M+H]$^+$ calcd. for C$_{13}$H$_9$NB: 257.9918; found: 257.9912.

References

**$^1$H and $^{13}$C spectra for all products**

*Figure 1* 400 MHz $^1$H NMR spectrum of compound 3 in CDCl$_3$

*Figure 2* 100 MHz $^{13}$C NMR spectrum of compound 3 in CDCl$_3$
Figure 3  400 MHz $^1$H NMR spectrum of compound 5 in CDCl$_3$.

Figure 4  100 MHz $^{13}$C NMR spectrum of compound 5 in CDCl$_3$. 
Figure 5  400 MHz $^1$H NMR spectrum of compound 7 in CDCl$_3$

Figure 6  400 MHz $^1$H NMR spectrum of compound 7 in CDCl$_3$
Figure 7 400 MHz $^1$H NMR spectrum of compound 9 in CDCl$_3$

Figure 8 400 MHz $^1$H NMR spectrum of compound 9 in CDCl$_3$
Figure 9 400 MHz $^1$H NMR spectrum of compound 11 in CDCl$_3$

Figure 10 400 MHz $^1$H NMR spectrum of compound 11 in CDCl$_3$
Figure 11  400 MHz $^1$H NMR spectrum of compound 13 in CDCl$_3$

Figure 12  100 MHz $^{13}$C NMR spectrum of compound 13 in CDCl$_3$
Figure 13 400 MHz $^1$H NMR spectrum of compound 15 in CDCl$_3$

Figure 14 100 MHz $^{13}$C NMR spectrum of compound 15 in CDCl$_3$
Figure 15 400 MHz $^1$H NMR spectrum of compound 17 in CDCl$_3$

Figure 16 100 MHz $^{13}$C NMR spectrum of compound 17 in CDCl$_3$
Figure 17 400 MHz $^1$H NMR spectrum of compound 19 in CDCl$_3$

Figure 18 100 MHz $^{13}$C NMR spectrum of compound 19 in CDCl$_3$
Figure 19 400 MHz $^1$H NMR spectrum of compound 21 in CDCl$_3$

Figure 20 100 MHz $^{13}$C NMR spectrum of compound 21 in CDCl$_3$
Figure 21  400 MHz $^1$H NMR spectrum of compound 25 in CDCl$_3$

Figure 22  100 MHz $^{13}$C NMR spectrum of compound 25 in CDCl$_3$
Figure 23 400 MHz $^1$H NMR spectrum of compound 28a in CDCl$_3$.

Figure 24 100 MHz $^{13}$C NMR spectrum of compound 28a in CDCl$_3$. 
Figure 25 400 MHz $^1$H NMR spectrum of compound 32 in CDCl$_3$

Figure 26 100 MHz $^{13}$C NMR spectrum of compound 32 in CDCl$_3$
**Figure 27** 400 MHz $^1$H NMR spectrum of compound 34 in CDCl$_3$

**Figure 28** 100 MHz $^{13}$C NMR spectrum of compound 34 in CDCl$_3$
Figure 29  400 MHz $^1$H NMR spectrum of compound 36 in CDCl$_3$

Figure 30  100 MHz $^{13}$C NMR spectrum of compound 36 in CDCl$_3$
Figure 31 400 MHz $^1$H NMR spectrum of compound 38 in CDCl$_3$

Figure 32 100 MHz $^{13}$C NMR spectrum of compound 38 in CDCl$_3$
Figure 33 400 MHz $^1$H NMR spectrum of compound 40 in CDCl$_3$

Figure 34 100 MHz $^{13}$C NMR spectrum of compound 40 in CDCl$_3$
Figure 35 400 MHz $^1$H NMR spectrum of compound 42 in CDCl$_3$

Figure 36 100 MHz $^{13}$C NMR spectrum of compound 42 in CDCl$_3$
Figure 37 400 MHz $^1$H NMR spectrum of compound 44 in CDCl$_3$

Figure 38 100 MHz $^{13}$C NMR spectrum of compound 44 in CDCl$_3$