Synthesis of 1,2,4-benzotriazines via 
CuI/1H-pyrrole-2-carboxylic acid catalyzed coupling of 
o-haloacetanilides and N-Boc hydrazine

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Supporting information

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4. $^1$H and $^{13}$C NMR spectra of compounds (8a-10j)
1. General remarks

All solvents were purified and dried prior to use. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Avance 500 MHz, and assigned in parts per million (δ). $^1$H NMR chemical shifts were given on the δ scale (ppm) and were referenced to internal TMS. Reference peaks for chloroform in $^{13}$C NMR spectra were set at 77.0 ppm. Low-resolution mass spectra were recorded on a LCMS-2010EV instrument (ESI). High-resolution mass spectra were recorded on an IonSpec 4.7 Tesla FTMS instrument. Silica gel plate GF254 were used for thin layer chromatography (TLC) and silica gel H or 300-400 mesh were used for flash column chromatography.

2. Experimental procedure

1. Experimental procedure for synthesis of aromatic azo compounds.

A Schlenk tube was charged with 2-iodoacetanilide 4 (0.5 mmol), N-Boc hydrazine (70 mg, 0.53 mmol), CuI (5 mg, 0.025 mmol), $^1$H-pyrrole-2-carboxylic acid (9 mg, 0.08 mmol), sodium iodide (15 mg, 0.1 mmol) and K$_2$CO$_3$ (138 mg, 1.0 mmol), evacuated and backfilled with argon. DMSO (1.5 mL) was successively added. The reaction mixture was stirred at 25 °C for 24-30 hours. Then the oxygen was introduced and the reaction mixture was stirred at 25 °C for 3-5 hours. The mixture was extracted by EtOAc (3* 10 mL). The combined organic phase was washed with brine and dried over Na$_2$SO$_4$. After concentration in vacuo, the residue was purified by column chromatography on silica gel to provide the desired product 9.

2. Experimental procedure for synthesis of substituted benzo[e][1,2,4]triazines.

To a solution of aromatic azo compounds (0.2 mmol) in CH$_2$Cl$_2$ (2.0 mL) was added TFA (0.5 mL). The solution was stirred at room temperature for 2 hours. Then aq. NaHCO$_3$ (5 mL) was added and the mixture was extracted by CH$_2$Cl$_2$ (3* 5 mL). The organic phase was dried over Na$_2$SO$_4$, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel to provide desired product 10.
3. Characterized data

**tert-Butyl 2-(2-butyramidophenyl)hydrazine-1-carboxylate (8a).** $^1$H NMR (500 MHz, CDCl$_3$) δ 8.60 (s, 1H), 7.27 (t, $J = 3.5$ Hz, 1H), 7.04 (d, $J = 7.1$ Hz, 1H), 6.93 – 6.81 (m, 2H), 6.50 (s, 1H), 6.36 (s, 1H), 2.08 (t, $J = 7.4$ Hz, 2H), 1.53 - 1.60 (m, 2H), 1.49 (s, 9H), 0.89 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 172.63, 156.68, 140.61, 126.06, 124.88, 121.63, 114.68, 81.08, 38.26, 28.28(3C), 18.95, 13.74. ESI-MS m/z 316.3 (M+Na)$^+$; ESI-HRMS m/z calcd for C$_{15}$H$_{24}$N$_3$O$_3$ (M+H)$^+$ 294.1812, found 294.1811.

![8a](image)

**tert-Butyl (E)-2-(2-butyramidophenyl)diazene-1-carboxylate (9a).** red liquid, 122 mg, 84 % yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 9.54 (s, 1H), 8.70 (dd, $J = 8.5$, 1.1 Hz, 1H), 7.74 (dd, $J = 8.2$, 1.5 Hz, 1H), 7.54 (ddd, $J = 8.6$, 7.5, 1.5 Hz, 1H), 7.09 (dd, $J = 8.4$, 7.3, 1.3 Hz, 2H), 2.41 (t, $J = 7.4$ Hz, 2H) 1.80 – 1.72 (m, 2H), 1.65 (s, 9H), 1.00 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 171.66, 160.23, 138.25, 138.05, 136.01, 123.11, 120.55, 119.36, 84.97, 40.16, 27.85 (3C), 18.75, 13.68. ESI-MS m/z 314.2 (M+Na)$^+$; ESI-HRMS m/z calcd for C$_{15}$H$_{24}$N$_3$O$_3$ (M+H)$^+$ 292.1656, found 292.1653.

![9a](image)

**tert-Butyl (E)-2-(2-acetamidophenyl)diazene-1-carboxylate (9b).** red liquid, 88 mg, 67 % yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 9.42 (s, 1H), 8.64 (d, $J = 8.5$ Hz, 1H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.52 (dd, $J = 8.3$, 7.4 Hz, 1H), 7.07 (dd, $J = 8.1$, 7.3 Hz, 1H), 2.21 (s, 3H), 1.64 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 168.62, 160.34, 138.49, 138.04, 135.95, 123.18, 120.53, 118.39, 85.04, 27.84, 25.22. ESI-MS m/z 286.2 (M+Na)$^+$; ESI-HRMS m/z calcd for C$_{13}$H$_{18}$N$_3$O$_3$ (M+H)$^+$ 264.1343, found 264.1343.
**tert-Butyl (E)-2-(2-isobutyramidophenyl)diazene-1-carboxylate (9c).** red liquid, 113 mg, 78 % yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.72 (s, 1H), 8.69 (dd, J = 8.5, 1.1 Hz, 1H), 7.75 (dd, J = 8.2, 1.5 Hz, 1H), 7.53 (ddd, J = 8.6, 7.5, 1.5 Hz, 1H), 7.09 (ddd, J = 8.4, 7.3, 1.3 Hz, 1H), 2.64 – 2.53 (m, 1H), 1.64 (s, 9H), 1.25 (d, J = 7.0 Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 175.68, 160.07, 138.18, 138.04, 136.00, 123.11, 120.53, 120.29, 84.89, 37.18, 27.83 (3C), 19.38 (2C). ESI-MS m/z 314.2 (M+Na)$^+$; ESI-HRMS m/z calcd for C$_{15}$H$_{22}$N$_3$O$_3$ $^+$ (M+H)$^+$ 292.1656, found 292.1653.

**tert-Butyl (E)-2-(2-pivalamidophenyl)diazene-1-carboxylate (9d).** red liquid, 110 mg, 72 % yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.24 (s, 1H), 8.70 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 7.10 (t, J = 7.7 Hz, 1H), 1.62 (s, 9H), 1.29 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 177.43, 159.66, 138.30, 137.36, 136.00, 123.08, 122.53, 120.31, 84.65, 40.41, 27.78 (3C), 27.41 (3C). ESI-MS m/z 306.2 (M+H)$^+$; ESI-HRMS m/z calcd for C$_{16}$H$_{24}$N$_3$O$_3$ $^+$ (M+H)$^+$ 306.1812, found 306.1811.

**tert-Butyl (E)-2-(2-(cyclopropanecarboxamido)phenyl)diazene-1-carboxylate (9e).** red liquid, 112 mg, 78 % yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.73 (s, 1H), 8.69 (dd, J = 8.5, 0.7 Hz, 1H), 7.76 (dd, J = 8.2, 1.5 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.12 – 7.07 (m, 1H), 1.68 (s, 9H), 1.66 – 1.60 (m, 1H), 1.15 – 1.10 (m, 2H), 0.93 – 0.88 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 172.37, 160.37, 138.61, 137.88, 136.11, 122.95, 120.54, 118.93, 85.06, 27.89 (3C), 16.51, 8.59 (2C). ESI-MS m/z 312.2 (M+Na)$^+$; ESI-HRMS m/z calcd for C$_{15}$H$_{20}$N$_3$O$_3$ $^+$ (M+H)$^+$ 290.1499, found 290.1497.
tert-Butyl (E)-2-((cyclohexanecarboxamido)phenyl)diazene-1-carboxylate (9f). red liquid, 129 mg, 78 % yield. ¹H NMR (500 MHz, CDCl₃) δ 9.79 (s, 1H), 8.71 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.10 (t, J = 7.7 Hz, 1H), 2.31 (tt, J = 11.6, 3.3 Hz, 1H), 1.99 (d, J = 11.9 Hz, 2H), 1.81 (dd, J = 10.0, 3.0 Hz, 2H), 1.73 – 1.61 (m, 10H), 1.51 (qd, J = 12.5, 2.8 Hz, 2H), 1.37 – 1.18 (m, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 174.85, 159.96, 138.19, 137.89, 136.02, 123.07, 120.92, 120.55, 84.81, 46.82, 29.48 (2C), 27.85 (3C), 25.70, 25.61 (2C). ESI-MS m/z 354.3 (M+Na)⁺; ESI-HRMS m/z calcd for C₁₈H₂₆N₃O₃⁺ (M+H)⁺ 332.1969, found 332.1968.

tert-Butyl (E)-2-((tetrahydro-2H-pyran-4-carboxamido)phenyl)diazene-1-carboxylate (9g). red liquid, 114 mg, 69 % yield. ¹H NMR (500 MHz, CDCl₃) δ 9.89 (s, 1H), 8.72 (d, J = 8.5 Hz, 1H), 7.83 (dd, J = 8.1, 1.2 Hz, 1H), 7.58 (dd, J = 8.4, 7.3 Hz, 1H), 7.16 (dd, J = 8.2, 2.1, 1.1 Hz, 1H), 4.06 (dt, J = 11.7, 3.2 Hz, 1H), 3.55 – 3.41 (m, 1H), 2.64 – 2.53 (m, 1H), 1.93 – 1.88 (m, 1H), 1.68 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 173.01, 159.77, 138.23, 137.48, 136.13, 123.42, 121.42, 120.57, 85.02, 67.16 (2C), 43.57, 29.04 (2C), 27.87 (3C). ESI-MS m/z 356.2 (M+Na)⁺; ESI-HRMS m/z calcd for C₁₇H₂₄N₃O₄⁺ (M+H)⁺ 334.1761, found 334.1759.

tert-Butyl (E)-2-((benzyl oxy)acetamido)phenyl)diazene-1-carboxylate (9h). red liquid, 136 mg, 74 % yield. ¹H NMR (500 MHz, CDCl₃) δ 10.45 (s, 1H), 8.73 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.59 – 7.51 (m, 1H), 7.36 (t, J = 6.1 Hz, 4H), 7.33 – 7.27 (m, 1H), 7.13 (ddd, J = 8.1, 5.0, 2.4 Hz, 1H), 4.67 (d, J = 1.5 Hz, 2H), 4.12 (s, 2H), 1.61 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 168.20, 160.59, 138.67, 137.67, 136.55, 135.71, 128.68 (2C),
128.18, 127.83 (2C), 123.65, 120.57, 118.08, 84.84, 73.59, 69.68, 27.85 (3C). ESI-MS m/z 392.2 (M+Na)+; ESI-HRMS m/z calc'd for C_{20}H_{24}N_{3}O_{4} (M+H)+ 370.1761, found 370.1759.

**tert-Butyl (E)-2-(2-acrylamidophenyl)diazene-1-carboxylate (9i).** red liquid, 80 mg, 58 % yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 9.76 (s, 1H), 8.77 (dd, \(J = 8.5, 0.9\) Hz, 1H), 7.77 (dd, \(J = 8.2, 1.5\) Hz, 1H), 7.60 – 7.53 (m, 1H), 7.15 – 7.11 (m, 1H), 6.43 (ddd, \(J = 17.0, 3.4, 1.0\) Hz, 1H), 6.30 (dd, \(J = 17.0, 10.2\) Hz, 1H), 5.80 (dd, \(J = 10.2, 1.0\) Hz, 1H), 1.66 (s, 9H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 163.67, 160.11, 138.23, 138.02, 136.04, 131.66, 128.07, 123.52, 120.69, 119.77, 85.09, 27.86 (3C). ESI-MS m/z 298.2 (M+Na)+; ESI-HRMS m/z calc'd for C_{14}H_{18}N_{3}O_{3} (M+H)+ 276.1343, found 276.1340.

**tert-Butyl (E)-2-(2-benzamidophenyl)diazene-1-carboxylate (9j).** red solid, 69 mg, 42 % yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 11.02 (s, 1H), 8.94 (dd, \(J = 8.5, 1.1\) Hz, 1H), 8.00 – 7.96 (m, 2H), 7.95 (dd, \(J = 8.1, 1.6\) Hz, 1H), 7.67 – 7.62 (m, 1H), 7.61 – 7.56 (m, 1H), 7.54 – 7.49 (m, 2H), 7.23 (ddd, \(J = 8.3, 7.4, 1.2\) Hz, 1H), 1.70 (s, 9H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 165.63, 159.41, 138.37, 136.95, 136.25, 134.46, 132.24, 128.81 (2C), 127.37 (2C), 124.25, 123.54, 120.48, 84.91, 27.89 (3C). ESI-MS m/z 348.3 (M+Na)+; ESI-HRMS m/z calc'd for C_{18}H_{20}N_{3}O_{3} (M+H)+ 326.1499, found 326.1498.

**tert-Butyl (E)-2-(2-(thiophene-2-carboxamido)phenyl)diazene-1-carboxylate (9k).** red solid, 69 mg, 42 % yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 11.10 (s, 1H), 8.83 (dd, \(J = 8.5, 1.1\) Hz, 1H), 7.95 (dd, \(J = 8.1, 1.6\) Hz, 1H), 7.71 (dd, \(J = 3.8, 1.1\) Hz, 1H), 7.62 (dd, \(J = 7.3, 1.4\) Hz, 1H), 7.59 (dd, \(J = 5.0, 1.0\) Hz, 1H), 7.22 (dd, \(J = 8.3, 7.4, 1.2\) Hz, 1H), 7.14 (dd, \(J = 5.0, 3.8\) Hz, 1H), 1.71 (s, 9H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 160.30, 159.14, 139.74, 138.01,
136.45, 136.30, 131.71, 128.83, 127.88, 125.30, 123.50, 120.31, 84.95, 27.88 (3C). ESI-MS m/z 354.2 (M+Na); ESI-HRMS m/z calcld for C_{16}H_{18}N_{3}O_{3}S^+ (M+H)^+ 332.1063, found 332.1061.

**tert-Butyl (E)-2-(2-butyramido-5-methylphenyl)diazene-1-carboxylate (9l).** red liquid, 131 mg, 86 % yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 9.39 (s, 1H), 8.57 (d, $J = 8.6$ Hz, 1H), 7.55 (s, 1H), 7.37 (d, $J = 8.6$ Hz, 1H), 2.40 (t, $J = 7.5$ Hz, 2H), 2.30 (s, 3H), 1.80 – 1.70 (m, 2H), 1.65 (s, 9H), 1.00 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 171.45, 160.24, 138.02, 137.02, 136.29, 132.94, 120.46, 118.70, 84.84, 40.10, 27.85 (3C), 20.55, 18.77, 13.69. ESI-MS m/z 306.2 (M+H)$^+$; ESI-HRMS m/z calcld for C$_{16}$H$_{24}$N$_3$O$_3^+$ (M+H)$^+$ 306.1812, found 306.1812.

**tert-Butyl (E)-2-(2-butyramido-5-methoxyphenyl)diazene-1-carboxylate (9m).** red liquid, 130 mg, 81 % yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 9.16 (s, 1H), 8.59 (d, $J = 9.1$ Hz, 1H), 7.17 (d, $J = 3.0$ Hz, 1H), 7.15 (dd, $J = 9.1$, 3.0 Hz, 1H), 3.77 (s, 3H), 2.38 (t, $J = 7.4$ Hz, 2H), 1.78 – 1.69 (m, 2H), 1.65 (s, 9H), 0.99 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 171.10, 160.40, 155.43, 138.76, 133.54, 124.37, 122.01, 99.53, 84.94, 55.56, 39.99, 27.85 (3C), 18.81, 13.68. ESI-MS m/z 344.3 (M+Na)$^+$; ESI-HRMS m/z calcld for C$_{16}$H$_{24}$N$_3$O$_4^+$ (M+H)$^+$ 322.1761, found 322.1759.

**tert-Butyl (E)-2-(2-butyramido-5-(methoxycarbonyl)phenyl)diazene-1-carboxylate (9n).** red liquid, 85 mg, 49 % yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.61 (s, 1H), 8.78 (d, $J = 8.9$ Hz, 1H), 8.40 (d, $J = 1.9$ Hz, 1H), 8.18 (dd, $J = 8.9$, 1.9 Hz, 1H), 3.88 (s, 3H), 2.43 (t, $J = 7.4$ Hz, 2H), 1.82 – 1.69 (m, 2H), 1.65 (s, 9H), 0.99 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$)
tert-Butyl (E)-2-(2-butyramido-5-fluorophenyl)diazene-1-carboxylate (9o). red liquid, 86 mg, 57 % yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 9.15 (s, 1H), 8.71 (dd, $J = 9.3$, 5.2 Hz, 1H), 7.40 (dd, $J = 8.8$, 3.0 Hz, 1H), 7.31 – 7.25 (m, 1H), 2.41 (t, $J = 7.5$ Hz, 2H), 1.81 – 1.71 (m, 2H), 1.66 (s, 9H), 1.00 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 171.36, 160.15, 158.27 (d, $J = 246.5$ Hz), 138.75 (d, $J = 6.3$ Hz), 135.54 (d, $J = 2.6$ Hz), 122.77 (d, $J = 23.1$ Hz), 122.27 (d, $J = 7.4$ Hz), 103.54 (d, $J = 23.9$ Hz), 85.45, 39.96, 27.84 (3C), 18.74, 13.66. ESI-MS $m/z$ 310.2 (M+H)$^+$; ESI-HRMS $m/z$ calcd for C$_{15}$H$_{21}$FN$_3$O$_3$ $(M+H)^+$ 310.1561, found 310.1564.

![Chemical Structure](image)

**3-Propylbenzo[e][1,2,4]triazine (10a).** yellow solid, 31.5 mg, 91 % yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.49 (d, $J = 8.4$ Hz, 1H), 7.99 (d, $J = 7.9$ Hz, 1H), 7.96 – 7.90 (m, 1H), 7.83 – 7.77 (m, 1H), 3.35 (t, $J = 9.6$ Hz, 2H), 2.08 – 1.97 (m, 2H), 1.06 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 166.45, 146.18, 140.85, 135.25, 129.82, 129.53, 128.51, 39.69, 22.28, 13.92. ESI-MS $m/z$ 174.1 (M+H)$^+$; ESI-HRMS $m/z$ calcd for C$_{10}$H$_{12}$N$_3^+$ (M+H)$^+$ 174.1026,
3-Methylbenzo[e][1,2,4]triazine (10b). yellow solid, 26 mg, 90 % yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.51 – 8.45 (d, $J = 8.3$ Hz, 1H), 7.98 – 7.89 (m, 2H), 7.80 (ddd, $J = 8.2$, 6.4, 1.7 Hz, 1H), 3.12 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 163.36, 145.97, 140.71, 135.40, 129.87, 129.51, 128.30, 24.24. ESI-MS $m/z$ 146.1 (M+H)$^+$; ESI-HRMS $m/z$ calcd for C$_8$H$_8$N$_3^+$ (M+H)$^+$ 146.0713, found 146.0713.

3-(tert-Butyl)benzo[e][1,2,4]triazine (10c). yellow solid, 35.5 mg, 95 % yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.51 (ddd, $J = 8.5$, 1.3, 0.6 Hz, 1H), 8.04 (ddd, $J = 8.6$, 1.2, 0.6 Hz, 1H), 7.94 (ddd, $J = 8.5$, 6.8, 1.4 Hz, 1H), 7.81 (ddd, $J = 10.3$, 5.8, 2.4 Hz, 1H), 1.64 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 172.20, 145.76, 140.54, 134.87, 129.71, 129.36, 128.91, 39.08, 29.64 (3C). ESI-MS $m/z$ 188.2 (M+H)$^+$; ESI-HRMS $m/z$ calcd for C$_{11}$H$_{14}$N$_3^+$ (M+H)$^+$ 188.1182, found 188.1181.

3-Cyclopropylbenzo[e][1,2,4]triazine (10d). yellow solid, 30.5 mg, 89 % yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.44 (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 3.6$ Hz, 2H), 7.76 – 7.70 (m, 1H), 2.70 (ddd, $J = 12.9$, 8.4, 4.8 Hz, 1H), 1.42 (dt, $J = 8.2$, 4.3 Hz, 2H), 1.32 – 1.25 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 167.42, 146.35, 140.97, 135.23, 129.56, 129.12, 128.20, 17.22, 11.89 (2C). ESI-MS $m/z$ 172.1 (M+H)$^+$; ESI-HRMS $m/z$ calcd for C$_{10}$H$_{10}$N$_3^+$ (M+H)$^+$ 172.0869, found 172.0867.

3-Cyclohexylbenzo[e][1,2,4]triazine (10e). yellow solid, 41 mg, 96 % yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.49 (d, $J = 7.8$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 7.93 (t, $J = 7.5$ Hz, 1H), 7.64 – 7.57 (m, 1H), 7.44 (m, 1H), 7.35 – 7.25 (m, 1H), 1.75 – 1.68 (m, 1H), 1.25 – 1.13 (m, 2H), 1.09 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 165.07, 145.45, 140.68, 135.59, 130.00, 129.52, 128.25, 127.51, 21.24, 14.60 (2C). ESI-MS $m/z$ 190.2 (M+H)$^+$; ESI-HRMS $m/z$ calcd for C$_{12}$H$_{14}$N$_3^+$ (M+H)$^+$ 190.1181, found 190.1181.

Found 174.1025.
7.80 (t, J = 7.8 Hz, 1H), 3.41 (tt, J = 11.7, 3.4 Hz, 1H), 2.17 (dd, J = 13.5, 1.7 Hz, 2H), 1.93 (ddd, J = 15.1, 7.6, 4.4 Hz, 2H), 1.89 – 1.79 (m, 3H), 1.52 (qt, J = 12.3, 3.2 Hz, 2H), 1.44 – 1.36 (m, 1H). 13C NMR (125 MHz, CDCl3) δ 169.53, 146.33, 140.95, 135.07, 129.70, 129.49, 128.66, 46.04, 31.94 (2C), 26.25 (2C), 25.90. ESI-MS m/z 214.2 (M+H)+; ESI-HRMS m/z calc'd for C13H16N3+ (M+H)+ 214.1339, found 214.1337.

3-(Tetrahydro-2H-pyran-4-yl)benzo[e][1,2,4]triazine (10f). yellow solid, 38 mg, 88 % yield. 1H NMR (500 MHz, CDCl3) δ 8.52 (dd, J = 8.4, 0.6 Hz, 1H), 8.06 – 8.01 (m, 1H), 7.97 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.84 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 4.21 – 4.14 (m, 2H), 3.68 (tt, J = 11.5, 3.8 Hz, 3H), 2.28 – 2.23 (m, 1H), 2.20 (dd, J = 11.7, 4.4 Hz, 1H), 2.17 – 2.11 (m, 2H). 13C NMR (125 MHz, CDCl3) δ 167.68, 146.47, 140.93, 135.33, 130.07, 129.53, 128.72, 67.80 (2C), 42.88, 31.37 (2C). ESI-MS m/z 216.2 (M+H)+; ESI-HRMS m/z calc'd for C13H14N3O+ (M+H)+ 216.1131, found 216.1130.

3-Phenylbenzo[e][1,2,4]triazine (10g). yellow solid, 38 mg, 92 % yield. 1H NMR (500 MHz, CDCl3) δ 8.81 – 8.74 (m, 2H), 8.55 (dd, J = 8.4, 0.6 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.98 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.85 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.64 – 7.56 (m, 3H). 13C NMR (125 MHz, CDCl3) δ 159.84, 146.48, 141.08, 135.62, 135.48, 131.45, 130.15, 129.59, 129.14, 128.94(2C), 128.77(2C). ESI-MS m/z 208.1 (M+H)+; ESI-HRMS m/z calc'd for C13H10N3O+ (M+H)+ 208.0869, found 208.0868.

3-(Thiophen-2-yl)benzo[e][1,2,4]triazine (10h). yellow solid, 39 mg, 91 % yield. 1H NMR (500 MHz, CDCl3) δ 8.46 (dd, J = 8.4, 0.7 Hz, 1H), 8.35 (dd, J = 3.7, 1.1 Hz, 1H), 8.02 – 7.97 (m, 1H), 7.92 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.76 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.61 (dd, J = 5.0, 1.1 Hz, 1H), 7.24 (dd, J = 4.9, 3.7 Hz, 1H). 13C NMR (125 MHz, CDCl3) δ 157.36, 146.00, 140.87, 140.72, 135.72, 131.31, 130.61, 129.75, 129.70, 128.65, 128.61. ESI-MS m/z
214.1 (M+H)$^+$; ESI-HRMS $m/z$ calcd for C$_{11}$H$_{8}$N$_3$S$^+$ (M+H)$^+$ 214.0433, found 214.0432.

![10i]

**7-Methyl-3-propylbenzo[e][1,2,4]triazine (10i).** yellow solid, 35 mg, 93 % yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.24 (s, 1H), 7.89 (d, $J$ = 8.7 Hz, 1H), 7.77 (dd, $J$ = 8.7, 1.6 Hz, 1H), 3.34 (t, $J$ = 7.5 Hz, 2H), 2.63 (s, 3H), 2.07 – 1.98 (m, 2H), 1.06 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.95, 146.22, 140.57, 139.60, 137.87, 127.95, 127.71, 39.61, 22.31, 21.87, 13.92. ESI-MS $m/z$ 188.2 (M+H)$^+$; ESI-HRMS $m/z$ calcd for C$_{11}$H$_{14}$N$_3$ (M+H)$^+$ 188.1182, found 188.1181.

![10j]

**Methyl 3-propylbenzo[e][1,2,4]triazine-7-carboxylate (10j).** yellow solid, 40 mg, 86 % yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.21 (d, $J$ = 1.8 Hz, 1H), 8.52 (dd, $J$ = 8.9, 1.9 Hz, 1H), 8.05 (d, $J$ = 8.8 Hz, 1H), 4.05 (s, 3H), 3.40 (t, $J$ = 7.6 Hz, 2H), 2.05 (dd, $J$ = 15.1, 7.5 Hz, 2H), 1.08 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.59, 165.36, 145.44, 142.55, 134.45, 132.32, 131.33, 129.02, 52.89, 39.76, 22.07, 13.91. ESI-MS $m/z$ 232.1 (M+H)$^+$; ESI-HRMS $m/z$ calcd for C$_{12}$H$_{14}$N$_3$O$_2$ (M+H)$^+$ 232.1081, found 232.1079.

**Reference**

(500 MHz, CDCl₃)
(500 MHz, CDCl3)