Experimental

$^1$H-NMR spectra were recorded on Bruker DPX-400 (400 MHz) or Bruker Nanobay (400 MHz) spectrometers using tetramethylsilane (SiMe$_4$, $\delta_H = 0.00$ ppm); CDCl$_3$ (CDCl$_3$, $\delta_H = 7.26$ ppm); or the central resonance of DMSO (DMSO, $\delta_H = 2.50$ ppm) as internal reference. $^{13}$C-NMR spectra were recorded on Bruker DPX-400 (100 MHz) or Bruker Nanobay (100 MHz) spectrometers using the central resonance of CDCl$_3$ (CDCl$_3$, $\delta_C = 77.00$ ppm) or the central resonance of DMSO (DMSO, $\delta_C = 39.43$ ppm) as the internal reference.

Assignments were made using a range of NMR experiments (DEPT135, COSY, HMQC and HMBC). All chemical shifts are quoted in parts per million (ppm) down-field from tetramethylsilane, measured from the centre of the resonance except in the case of multiplets of more than one proton that are quoted as a range. Coupling constants are quoted to the nearest 0.2 Hz. Splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin.), septet (sept.), multiplet (m) ap. (apparent), broad (b) and combinations thereof.

Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer as a thin film.

Pet. ether refers to the fraction of light petroleum ether boiling between 40 and 60 °C All reagents were used as obtained from commercial sources unless otherwise stated.

Melting points were obtained using a Stuart SMP10 melting point apparatus and are uncorrected.

Analytical thin layer chromatography (TLC) was performed using pre-coated Merck aluminium backed silica gel plates (Silica gel 60 F$_{254}$). Visualisation was by UV light and/or treatment with acidic potassium permanganate, ninhydrin or acidic ammonium molybdate (IV).
Step 1: Formation of Hydrazine

Methyl (E)-2-(1-phenylethylidene)hydrazine-1-carboxylate

![Chemical Structure](image)

Acetophenone (8.0 g, 67 mmol) was dissolved in EtOH (25 mL). Enough water was added to make the solution become cloudy, then more EtOH was added dropwise until the solution clarified. Methyl hydrazinocarboxylate (7.8 g, 87 mmol) was then added, followed by glacial acetic acid (30 drops). The reaction was heated at reflux 30 minutes, allowed to cool, then further cooled on ice. The resulting solid was collected by Büchner filtration, washed with a minimum volume of 95% EtOH then dried in a vacuum oven to afford methyl (E)-2-(1-phenylethylidene)hydrazine-1-carboxylate as a colourless solid (12 g, 64 mmol, 96%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 (1H, br s, NH), 7.75–7.73 (2H, m, CH$_{ar}$), 7.37–7.35 (3H, m, CH$_{ar}$), 3.87 (3H, s, OCH$_3$), 2.22 (3H, s, CH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.8 (C=N), 138.0 (C$_{ar}$), 129.2 (C$_{ar}$H), 128.4 (C$_{ar}$H), 126.3 (C$_{ar}$H), 53.1 (OCH$_3$), 13.1 (CH$_3$).

The resonance for C=O was not present due to line broadening.

$\nu$ max (neat) cm$^{-1}$ 3203, 3039, 2950, 1731, 1704, 1537, 1490, 1444, 1429.

HRMS (+ESI) m/z [(M+H)$^+$] found 193.0972, C$_{10}$H$_{13}$O$_2$N$_2$ requires 193.0972.

m.p. (EtOH) 134–135 °C
Methyl (E)-2-(1-(4-bromophenyl)ethylidene)hydrazine-1-carboxylate

4-Bromoacetophenone (1.0 g, 5.0 mmol) was dissolved in EtOH (10 mL). Enough water was added to make the solution become cloudy, then more EtOH was added dropwise until the solution clarified. Methyl hydrazinocarboxylate (0.59 g, 6.5 mmol) was then added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux 30 minutes, allowed to cool, then placed on ice. The resulting solid was collected by Büchner filtration, washed with a minimum volume of 95% EtOH then dried in a vacuum oven to afford methyl (E)-2-(1-(4-bromophenyl)ethylidene)hydrazine-1-carboxylate as a colourless solid (1.1 g, 4.1 mmol, 80%).

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{)}\ \delta 7.98 (1\text{H, br s, NH}), 7.63 (2\text{H, d, } J = 8.8 \text{ Hz, } \text{CH}_2\text{Ar}), 7.49 (2\text{H, d, } J = 8.8 \text{ Hz, } \text{CH}_2\text{Ar}), 3.88 (3\text{H, s, OCH}_3), 2.19 (3\text{H, s, CH}_3).\]

\[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\text{)}\ \delta 147.5 (\text{C=N}), 136.8 (\text{C}_\text{ArBr}), 131.6 (\text{C}_\text{ArH}), 127.9 (\text{C}_\text{ArH}), 123.6 (\text{C}_\text{Ar}), 53.3 (\text{OCH}_3), 12.7 (\text{CH}_3).\]

The resonance for C=O was not present due to line broadening.

\(v_{\text{max}}\) (neat) cm\(^{-1}\) 3196, 2945, 1730, 1702, 1539, 1484.

HRMS (+ESI) \(m/z [(M+H)^+]\) found 271.0077 \(\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2\text{Br}\) requires 271.0077.

m.p. (EtOH) 152–155 °C
Methyl (E)-2-(2-methoxybenzylidene)hydrazine-1-carboxylate

2-Methoxybenzaldehyde (1.0 g, 7.3 mmol) was dissolved in EtOH (3.0 mL). Enough water was added to make the solution become cloudy, then more EtOH was added dropwise until the solution clarified. Methyl hydrazinocarboxylate (0.86 g, 9.6 mmol) was then added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux for 30 minutes, then allowed to cool. The resulting solid was collected by Büchner filtration, washed with a minimum volume of 95% EtOH then dried in a vacuum oven to afford methyl (E)-2-(2-methoxybenzylidene)hydrazine-1-carboxylate as a colourless solid (0.99 g, 4.8 mmol, 65%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.25 (2H, br s, NH and HC=N), 7.98 (1H, br s, CH$_{ar}$), 7.35–7.31 (1H, m, CH$_{ar}$), 6.96 (1H, t, $J = 7.6$ Hz CH$_{ar}$), 6.86 (1H, d, $J = 8.4$ Hz, CH$_{ar}$), 3.84 (6H, s, 2 × OCH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.8 (C$_{ar}$), 154.0 (C=O), 140.6 (C=N), 131.3 (C$_{a}$H), 126.8 (C$_{a}$H), 122.1 (C$_{a}$), 120.9 (C$_{a}$H), 110.8 (C$_{a}$H), 55.5 (OCH$_3$), 52.9 (OCH$_3$).

$\nu$ max (neat) cm$^{-1}$ 3208, 3063, 2952, 2839, 1711, 1598, 1546, 1433, 1246.

HRMS (+ESI) m/z [(M+H)$^+$] found 209.0921 C$_{10}$H$_{13}$O$_3$N$_2$ requires 209.0921.

m.p. (EtOH) 156–160 °C
Methyl 2-(diphenylmethylene)hydrazine-1-carboxylate

Benzophenone (1.0 g, 5.5 mmol) was dissolved in EtOH (10 mL). Methyl hydrazinocarboxylate (0.64 g, 7.1 mmol) was added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux overnight, then allowed to cool and the solvent removed in vacuo. The resulting oil was purified by flash column chromatography (30% EtOAc/40–60 pet. ether) to afford methyl 2-diphenylmethylene)hydrazine-1-carboxylate as a colourless solid (0.80 g, 3.1 mmol, 57%).

Major peaks reported. Minor peaks due to geometric isomers/rotamers.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (1H, br s, NH), 7.53–7.45 (6H, m, CH$_{ar}$), 7.37–7.25 (4H, m, CH$_{ar}$), 3.82 (3H, br s, OCH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.0 (C=N), 151.7 (C=O), 136.9 (C$_{ar}$), 131.8 (C$_{ar}$), 129.9 (C$_{ar}$H), 129.8 (C$_{ar}$H), 129.6 (C$_{ar}$H), 128.4 (C$_{ar}$H), 128.4 (C$_{ar}$H), 128.3 (C$_{ar}$H), 127.6 (C$_{ar}$H), 53.0 (OCH$_3$).

The resonances for C=N and C=O were not present due to line broadening.

$\nu_{max}$ (neat) cm$^{-1}$ 3350, 1751, 1489, 1444, 1324, 1210.

HRMS (+ESI) m/z [(M+Na)$^+$ found 277.0947 C$_{15}$H$_{14}$O$_2$N$_2$Na requires 277.0947].

m.p. (EtOH) 127–129 °C
p-Anisaldehyde (2.0 g, 15 mmol) was dissolved in EtOH (10 mL). Methyl hydrazinocarboxylate (1.7 g, 19 mmol) was added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux overnight, then allowed to cool, then placed on ice. The resulting solid was collected by Büchner filtration and washed with a minimum volume of 95% EtOH then dried in a vacuum oven to afford methyl (E)-2-(4-methoxybenzylidene)hydrazine-1-carboxylate as a colourless solid (2.4 g, 11 mmol, 77%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.45 (1H, br s, NH), 7.83 (1H, br s, HC=N), 7.61 (2H, d, $J$ = 8.7 Hz, CH$_{Ar}$), 6.87 (2H, d, $J$ = 8.7 Hz, CH$_{Ar}$), 3.81 (6H, m, 2 × OCH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.2 (C$_{Ar}$OMe), 154.4 (C=O), 144.8 (C=N), 128.8 (C$_{Ar}$H), 126.4 (C$_{Ar}$), 114.1 (C$_{Ar}$H), 55.3 (OCH$_3$), 52.7 (OCH$_3$).

$\nu_{\text{max}}$ (neat) cm$^{-1}$ 3250, 3006, 2928, 2837, 1731, 1711, 1607, 1540, 1511.

HRMS (+ESI) m/z [(M+Na)$^+$] found 231.0740 C$_{10}$H$_{12}$O$_3$N$_2$Na requires 231.0740.

m.p. (EtOH) 141–144 °C
Methyl (E)-2-(4-chlorobenzylidene)hydrazine-1-carboxylate

\[
\text{Cl} \quad \text{N} \quad \text{N} \quad \text{O} \quad \text{Me}
\]

\(p\)-Chlorobenzaldehyde (0.59 g, 4.2 mmol) was dissolved in EtOH (5.0 mL). Methyl hydrazinocarboxylate (0.49 g, 5.4 mmol) was added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux overnight, then allowed to cool and the solvent removed \textit{in vacuo}. The resulting oil was purified by flash column chromatography, pre-adsorbing the crude material onto silica, (20–50% EtOAc/40–60 pet. ether) to afford methyl (E)-2-(4-chlorobenzylidene)hydrazine-1-carboxylate as a colourless solid (0.70 g, 3.3 mmol, 79%).

\(^1\text{H} \text{NMR} \ (400 \text{ MHz, CDCl}_3) \delta 8.23 \ (1\text{H, br s, NH}), 7.84 \ (1\text{H, br s, HC=N}), 7.61 \ (2\text{H, d, } J = 8.5 \text{ Hz, CH}_2\text{Ar}), 7.36 \ (2\text{H, d, } J = 8.5 \text{ Hz, CH}_2\text{Ar}), 3.77 \ (3\text{H, br s, OCH}_3)\).

\(^{13}\text{C} \text{NMR} \ (100 \text{ MHz, CDCl}_3) \delta 143.3 \ (\text{C=N}), 136.1 \ (\text{C}_2\text{Ar}), 132.2 \ (\text{C}_3\text{Ar}), 129.0 \ (\text{C}_4\text{H}), 128.4 \ (\text{C}_5\text{H}), 52.9 \ (\text{OCH}_3)\).

The resonance for C=O was not present due to line broadening.

\(\nu_{max} \text{ (neat) cm}^{-1} 3235, 3061, 2951, 1736, 1704, 1553, 1489, 1460, 1261\).

HRMS (+ESI) \text{m/z} [(\text{M+Na})^+] \text{found} 235.0245 \text{C}_9\text{H}_9\text{ClO}_2\text{N}_2\text{Na requires} 235.0245\).

m.p. (EtOH) 164–166 °C
Step 1

Supplementary information

Methyl \((E)-2-(1\text{-}naphthalen\text{-}2\text{-}yl)\text{ethylidene}\)hydrazine\text{-}1-carboxylate

![Chemical structure of methyl \((E)-2-(1\text{-}naphthalen\text{-}2\text{-}yl)\text{ethylidene}\)hydrazine\text{-}1-carboxylate](image)

2-Acetonaphthone (2.0 g, 12 mmol) was dissolved in EtOH (10 mL). Methyl hydrazinocarboxylate (1.4 g, 15 mmol) was added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux overnight, then allowed to cool, then placed on ice. The resulting solid was collected by Büchner filtration and washed with a minimum volume of 95% EtOH then dried in a vacuum oven to afford methyl \((E)-2-(1\text{-}naphthalen\text{-}2\text{-}yl)\text{ethylidene}\)hydrazine\text{-}1-carboxylate as a colourless solid (1.7 g, 7.0 mmol, 60%).

\(^1\text{H NMR (400 MHz, CDCl}_3\) δ 8.06 (3H, br app. s, NH and CH\(_{\text{Ar}}\)), 7.86–7.81 (3H, m, CH\(_{\text{Ar}}\)), 7.51–7.46 (2H, m, CH\(_{\text{Ar}}\)), 3.90 (3H, s, OCH\(_3\)), 2.31 (3H, s, CH\(_3\)).

\(^{13}\text{C NMR (100 MHz, CDCl}_3\) δ 154.4 (C=O), 148.3 (C=NH), 135.3 (C\(_{\text{Ar}}\)), 133.7 (C\(_{\text{Ar}}\)), 133.0 (C\(_{\text{Ar}}\)), 128.5 (C\(_{\text{Ar}}\)), 128.1 (C\(_{\text{Ar}}\)), 127.6 (C\(_{\text{Ar}}\)), 126.7 (C\(_{\text{Ar}}\)), 126.3 (C\(_{\text{Ar}}\)), 126.1 (C\(_{\text{Ar}}\)), 123.8 (C\(_{\text{Ar}}\)), 53.1 (OCH\(_3\)), 12.7 (CH\(_3\)).

\(\nu\text{max (neat) cm}^{-1}\) 3204, 2951, 1733, 1703, 1532, 1431, 1241, 1232.

HRMS (+ESI) \(m/z\) \([M+Na]^+\) found 265.0947 \(C_{14}H_{14}O_2N_2Na\) requires 265.0947.

m.p. (EtOH) 134–135 °C
Step 1

Supplementary information

Methyl (E)-2-(((4-methoxyphenyl)(phenyl)methylene)hydrazine-1-carboxylate

4-Methoxybenzophenone (2.0 g, 9.4 mmol) was dissolved in EtOH (10 mL). Methyl hydrazinocarboxylate (1.1 g, 12 mmol) was added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux overnight, then allowed to cool, and the solvent removed in vacuo. The resulting oil was purified by flash column chromatography, pre-adsorbing the crude material onto silica, (10–50% EtOAc/40–60 pet. ether) to afford methyl (E)-2-(((4-methoxyphenyl)(phenyl)methylene)hydrazine-1-carboxylate as a colourless solid (1.5 g, 5.2 mmol, 55%, or 87% brsm).

Product isolated as a mixture of 2 isomers. All major peaks are reported.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (1H, br s, NH), 7.73 (1H, br s, NH), 7.57–7.50 (7H, m, CH$_{Ar}$), 7.36–7.29 (2H, m, CH$_{Ar}$), 7.27–7.23 (2H, m, CH$_{Ar}$), 7.20–7.17 (2H, m, CH$_{Ar}$), 7.07–7.05 (2H, m, CH$_{Ar}$), 6.85–6.82 (2H, m, CH$_{Ar}$), 3.88 (3H, s, OCH$_3$), 3.80 (6H, br s, OCH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.8 (C$_{Ar}$), 160.6 (C$_{Ar}$), 154.0 (C$_{quat}$), 151.5 (C$_{quat}$), 137.3 (C$_{Ar}$), 132.1 (C$_{Ar}$), 129.9 (C$_{Ar}$), 129.8 (C$_{Ar}$), 129.7 (C$_{Ar}$), 129.6 (C$_{Ar}$), 129.5 (C$_{Ar}$), 129.1 (C$_{Ar}$), 128.4 (C$_{Ar}$), 128.2 (C$_{Ar}$), 127.7 (C$_{Ar}$), 123.6 (C$_{Ar}$), 115.2 (C$_{Ar}$), 113.6 (C$_{Ar}$), 55.4 (OCH$_3$), 55.3 (OCH$_3$), 52.9 (OCH$_3$).

$\nu_{\text{max}}$ (neat) cm$^{-1}$ 3361, 2957, 2840, 1747, 1610, 1498, 1443, 1245.

HRMS (+ESI) $m/z$ [(M+Na)$^+$] found 307.1053 C$_{16}$H$_{16}$O$_3$N$_2$Na requires 307.1053.

m.p. (EtOH) 112–113 °C
Step 1

**Methyl (E)-2-(2-methyl-1-phenylpropylidene)hydrazine-1-carboxylate**

Isobutyrophenone (2.0 g, 14 mmol) was dissolved in EtOH (10 mL). Methyl hydrazinocarboxylate (1.6 g, 18 mmol) was added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux overnight, allowed to cool and the solvent removed *in vacuo*. The resulting oil was purified by flash column chromatography, pre-adsorbing the crude material onto silica, (15–50% EtOAc/40–60 pet. ether) to afford methyl (E)-2-(2-methyl-1-phenylpropylidene)hydrazine-1-carboxylate as a colourless solid (2.1 g, 13 mmol, 96%).

\[\text{O} \quad \text{Me}\]
\[\text{N} \quad \text{NH}\]
\[\text{Ph}\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47–7.42 (4H, m, NH and CH\(_{Ar}\)), 7.12–7.10 (2H, m, CH\(_{Ar}\)), 3.77 (3H, s, OCH\(_3\)), 2.91 (1H, app. septet, \(J = 7.1\) Hz, CH), 1.11 (6H, d, \(J = 7.2\) Hz, CH\(_3\)).

\(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.0 (C=O), 153.2 (C=N), 131.3 (C\(_{Ar}\)), 128.4 (C\(_{Ar}\)H), 128.3 (C\(_{Ar}\)H), 126.4 (C\(_{Ar}\)H), 51.9 (OCH\(_3\)), 35.4 (CH(CH\(_3\))\(_2\)), 19.1 (CH(CH\(_3\))\(_2\)).

\(\nu_{\text{max}}\) (neat) cm\(^{-1}\) 3238, 2970, 2931, 1716, 1505, 1221.

HRMS (+ESI) m/z [(M+Na)*] found 243.1104 C\(_{12}\)H\(_{16}\)O\(_2\)N\(_2\)Na requires 243.1104.

m.p. (EtOAc/pet. ether) 85–88 °C
**4-(2-{(Methoxycarbonyl)hydrazono)-4-(naphthalen-2-yl)butanoic acid**

![Chemical Structure](image)

4-(naphthalen-2-yl)-4-oxobutanoic acid (1.0 g, 4.4 mmol) was suspended in hot ethanol (10 mL). Methyl hydrazinocarboxylate (0.55 g, 5.7 mmol) was then added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux overnight, allowed to cool, then further cooled on ice. The resulting solid was collected by Büchner filtration, washed with a minimum volume of 95% EtOH then dried in a vacuum oven to afford 4-(2-{(methoxycarbonyl)hydrazono)-4-(naphthalen-2-yl)butanoic acid as a tan solid (1.3 g, 4.2 mmol, 96 %). A mix of isomers was observed by NMR and was used crude in the Wolff-Kishner reduction step.

Very insoluble mixture of isomers. $^1$H NMR (DMSO-$d_6$) and TLC showed no starting material.

$\nu_{\text{max}}$ (neat) cm$^{-1}$ 3400br, 1724, 1585, 1459, 1226, 1075, 1033, 820, 751, 630.

HRMS (+ESI) $m/z$ [(M+H)$^+$] found 301.1184 C$_{16}$H$_{17}$O$_4$N$_2$ requires 301.1183].

m.p. (EtOH) >270 °C.
Step 1

**Supplementary information**

Methyl (E)-2-((3-methylthiophen-2-yl)methylene)hydrazine-1-carboxylate

3-Methylthiophene-2-carbaldehyde (1.7 mL, 16 mmol) was dissolved in EtOH (10 mL). Methyl hydrazinocarboxylate (1.9 g, 21 mmol) was added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux overnight, allowed to cool, then placed on ice. The resulting solid was collected by Büchner filtration and washed with the minimum volume of 95% EtOH then dried in a vacuum oven to afford methyl (E)-2-((3-methylthiophen-2-yl)methylene)hydrazine-1-carboxylate as a tan solid (1.8 g, 9.0 mmol, 57%).

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.30–8.20 (2H, br s, NH and HC=N), 7.27–7.24 (1H, m, CH}_x\text{), 6.82 (1H, d, J} = 4.8 \text{ Hz, CH}_x\text{), 3.74 (3H, s, OCH}_3\text{), 2.31 (3H, s, CH}_3\text{).} \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{)} \delta 139.5 (C}_x\text{), 132.1 (C}_x\text{), 130.5 (C}_x\text{H, 127.2 (C}_x\text{H, 52.9 (OCH}_3\text{), 13.9} \]

(CH}_3\text{).} \]

The resonances for C=N and C=O were not present due to line broadening.

\[ \text{v}_{\text{max}} \text{ (neat) cm}^{-1} 3216, 3066, 1725, 1703, 1557, 1444, 1339, 1261. \]

HRMS (+ESI) m/z [(M+Na)** found 221.0355 C_8H_{10}O_3N_2NaS requires 221.0355].

m.p. (EtOH) 151–153 °C
Methyl (E)-2-(1-(thiophen-2-yl)ethylidene)hydrazine-1-carboxylate

2-Acetylthiophene (1.7 mL, 16 mmol) was dissolved in EtOH (10 mL). Methyl hydrazinocarboxylate (1.9 g, 21 mmol) was added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux overnight, allowed to cool and the solvent removed in vacuo. The resulting oil was purified by flash column chromatography, pre-adsorbing the crude material onto silica, (30% EtOAc/40–60 pet. ether) to afford methyl (E)-2-(1-(thiophen-2-yl)ethylidene)hydrazine-1-carboxylate as a colourless solid (2.6 g, 13 mmol, 82%).

Product isolated as a mixture of 2 isomers. Major peaks are reported.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (1H, br s, NH), 7.32 (1H, dd, $J$ = 5.0, 0.8 Hz, CH$_{a_2}$), 7.27 (1H, dd, $J$ = 3.7, 1.1 Hz, CH$_{a_1}$), 7.00 (1H, dd, $J$ = 5.1, 3.8 Hz, CH$_{a_3}$), 3.87 (3H, s, OCH$_3$), 2.23 (3H, s, CH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.2 (C=O), 145.0 (C=N), 143.1 (C$_{a_2}$), 127.9 (C$_{a_1}$H), 127.1 (C$_{a_3}$H), 126.4 (C$_{a_4}$H), 53.2 (OCH$_3$), 13.4 (CH$_3$).

$\nu_{max}$ (neat) cm$^{-1}$ 3225, 3097, 2960, 1694, 1470, 1445.

HRMS (+ESI) m/z [(M+Na)$^+$ found 221.0355 C$_8$H$_{10}$O$_3$N$_2$NaS requires 221.0355].

m.p. (EtOAc/pet.) 134–136°C
Methyl (E)-2-(1-(pyridin-3-yl)ethylidene)hydrazine-1-carboxylate

3-Acetoylepyridine (1.8 mL, 17 mmol) was dissolved in EtOH (10 mL). Methyl hydrazinocarboxylate (1.9 g, 22 mmol) was added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux overnight, allowed to cool and water added until the solution became opaque. The flask was then placed on ice. The resulting solid was collected by Büchner filtration and washed with a minimum volume of 95% EtOH then dried in a vacuum oven to afford methyl (E)-2-(1-(pyridin-3-yl)ethylidene)hydrazine-1-carboxylate as a colourless solid (2.3 g, 11.9 mmol, 70%).

1H NMR (400 MHz, CDCl₃) δ 8.92 (1H, d, J = 2.0 Hz, CH₆), 8.60 (1H, dd, J = 4.8, 1.5 Hz, CH₆), 8.29 (1H, br s, NH), 8.12 (1H, d, J = 7.8 Hz, CH₆). 7.31 (1H, dd, J = 8.0 Hz, 4.8 Hz, CH₆), 3.89 (3H, s, OCH₃), 2.24 (3H, s, CH₃).

13C NMR (100 MHz, CDCl₃) δ 154.6 (C=O), 150.2 (C₆H), 147.6 (C₆H), 146.0 (C=H), 146.0 (C₆H), 133.7 (C₆H), 123.3 (C₆H), 53.3 (OCH₃), 12.8 (CH₃).

νmax (neat) cm⁻¹ 3197, 3076, 3012, 1742, 1619, 1532, 1482.

HRMS (+ESI) m/z [(M+H)+] found 194.0924 C₉H₁₂O₂N₃ requires 194.0924.

m.p. (EtOH) 148–150 °C
2-Acetyl-5-methylfuran (1.9 mL, 16 mmol) was dissolved in EtOH (10 mL). Methyl hydrazinocarboxylate (1.9 g, 21 mmol) was added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux overnight, allowed to cool and the solvent removed in vacuo. The resulting oil was purified by flash column chromatography, pre-adsorbing the crude material onto silica, (30% EtOAc/40–60 pet. ether) to afford methyl (E)-2-{1-(5-methylfuran-2-yl)ethylidene}hydrazine-1-carboxylate as a colourless solid (2.8 g, 14 mmol, 89%).

Isolated as a mixture of isomers. Major peaks are reported.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.08 (1H, br s, NH), 6.60 (1H, d, $J = 4.3$ Hz, CH$_{ar}$), 6.04 (1H, d, $J = 3.6$ Hz, CH$_{ar}$), 3.76 (3H, s, OCH$_3$), 2.42 (3H, s, CH$_3$), 2.09 (3H, s, CH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.8 (C$_{ar}$) 154.8 (C=O), 149.8 (C$_{ar}$), 141.0 (C=N), 112.4 (C$_{ar}$H), 107.9 (C$_{ar}$H), 53.3 (OCH$_3$), 13.9 (CH$_3$), 12.2 (CH$_3$).

$\nu_{\text{max}}$ (neat) cm$^{-1}$ 3250, 2949, 1718, 1553, 1520, 1446, 1263, 1237.

HRMS (+ESI) $m/z$ [(M+Na)$^+$ found 219.0740 C$_9$H$_{12}$O$_3$N$_2$Na requires 219.0740].

m.p. (EtOH) 119–120 °C
**Methyl (E)-2-(4-fluorobenzylidene)hydrazine-1-carboxylate**

\[
\text{OMe} \quad \text{N} \quad \text{H} \quad \text{F} \quad \text{Ar} \quad \text{N} \quad \text{H} \\
\]

\(\text{p-Fluorobenzaldehyde (1.0 g, 8.1 mmol)}\) was placed taken into \(\text{EtOH (3.0 mL)}\). Once dissolved, methyl hydrazinocarboxylate (0.94 g, 11 mmol) was added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux for 30 minutes, then allowed to cool to ambient temperature. Once cool, water was added to induce crystallization. The resulting solid was collected by Büchner filtration, washed with 95% EtOH then dried in a vacuum oven to afford methyl (E)-2-(4-fluorobenzylidene)hydrazine-1-carboxylate as a colourless solid (0.83 g, 4.2 mmol, 52%).

\(\begin{align*}
^1\text{H NMR (400 MHz, CDCl}_3\text{)} & \delta \ 8.71 \ (1\text{H, br s, NH}), \ 8.43 \ (1\text{H, br s, C=NH}), \ 7.68-7.64 \ (2\text{H, m, CH}_2\text{Ar}), \ 7.06 \ (2\text{H, t, } J = 8.6 \text{ Hz, CH}_2\text{Ar}), \ 3.75 \ (3\text{H, s, OCH}_3). \\
^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} & \delta \ 163.8 \ (d, J = 246 \text{ Hz, C}_\text{Ar}F), \ 154.8 \ (\text{C}=\text{O}), \ 143.5 \ (\text{C}=\text{N}), \ 129.9 \ (d, J = 3 \text{ Hz, C}_\text{Ar}), \ 129.1 \ (d, J = 8 \text{ Hz, C}_\text{Ar}), \ 115.8 \ (d, J = 22 \text{ Hz, C}_\text{ArH}), \ 53.1 \ (\text{OCH}_3). \\
^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}: \delta \ -109.9 \\
\nu_{\text{max}} \ (\text{neat}) \ cm^{-1} & \ 3158, \ 3028, \ 2996, \ 2823, \ 1697, \ 1601, \ 1564, \ 1463. \\
\text{HRMS (+ESI) } m/z [(\text{M}+\text{Na})^+ \text{ found 219.0540 } \text{C}_9\text{H}_9\text{FN}_2\text{O}_2\text{Na requires 219.0540}]. \\
\text{m.p. (EtOH) 122–124 °C}
\end{align*}\)
Methyl (E)-2-(3,5-di-tert-butyl-2-hydroxybenzylidene)hydrazine-1-carboxylate

3,5-Di-tert-butyl-2-hydroxybenzaldehyde (1.0 g, 4.3 mmol) was placed into EtOH (3.0 mL). Once dissolved, methyl hydrazinocarboxylate (0.50 g, 5.5 mmol) was added, followed by glacial acetic acid (5 drops). The reaction was heated at reflux for 30 minutes, then allowed to cool to ambient temperature. The resulting solid was collected by Büchner filtration, washed with 95% EtOH then dried in a vacuum oven to afford methyl (E)-2-(3,5-di-tert-butyl-2-hydroxybenzylidene)hydrazine-1-carboxylate as a colourless solid (0.89 g, 2.9 mmol, 67%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 11.1 (1H, s, HC=N), 8.85 (1H, br s, OH), 7.99 (1H, br s, NH), 7.36 (1H, d, $J = 2.4$ Hz, CH$_{ar}$), 7.00 (1H, d, $J = 2.0$ Hz, CH$_{ar}$), 3.88 (3H, br s, OCH$_3$), 1.44 (9H, s, CH$_3$), 1.29 (9H, s, CH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.3 (C$_{ar}$O), 141.1 (C$_{ar}$Bu), 137.0 (C$_{ar}$Bu), 126.5 (C$_{ar}$H), 125.3 (C$_{ar}$H), 116.4 (C$_{ar}$), 53.3 (OCH$_3$), 35.1 (C(CH$_3$)$_3$), 34.2 (C(CH$_3$)$_3$), 31.5 (C(CH$_3$)$_3$), 29.4 (C(CH$_3$)$_3$).

The resonances for C=N and C=O were not present due to line broadening.

$\nu_{\text{max}}$ (neat) cm$^{-1}$ 3117, 2960, 1704, 1615, 1445, 1343.

HRMS (+ESI) m/z [M+Na]$^+$ found 329.1836 C$_{17}$H$_{26}$O$_3$N$_2$Na requires 329.1836.

m.p. (EtOH) 200–206 °C
Step 2 - Reduction

Ethyl benzene

KOH (14 g, 250 mmol) was added to triethylene glycol (40 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (E)-2-(1-phenylethylidene)hydrazine-1-carboxylate (8.0 g, 42 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et₂O (2 × 50 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (100% pentane) to give ethyl benzene as a yellow oil (3.1 g, 29 mmol, 70%).

¹H NMR (400 MHz, CDCl₃): δ 7.29–7.17 (5H, m, CH₆Ar), 2.64 (2H, q, J = 7.6 Hz, CH₂CH₃), 1.24 (3H, t, J = 7.6 Hz, CH₂C₃H₃).

¹³C NMR (100 MHz, CDCl₃): δ 144.3 (C₆H), 128.3 (C₆H), 127.9 (C₆H), 125.6 (C₆H), 28.9 (CH₂CH₃), 15.6 (CH₂C₃H₃).

Data is in agreement with published data:

1-Bromo-4-ethylbenzene

KOH (0.42 g, 7.4 mmol) added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (E)-2-(1-(4-bromophenyl)ethylidene)hydrazine-1-carboxylate (0.5 g, 1.9 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et₂O (2 × 10 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (10% Et₂O/pentane) to give 1-bromo-4-ethylbenzene as a yellow oil (0.26 g, 1.3 mmol, 76%).

¹H NMR (400 MHz, CDCl₃) δ 7.83 (2H, d, J = 8.4 Hz, CH₂Ar), 7.06 (2H, d, J = 8.4 Hz, CH₂Ar), 2.59 (2H, q, J = 7.6 Hz, CH₂CH₃), 1.21 (3H, t, J = 7.6 Hz, CH₂CH₃).

¹³C NMR (100 MHz, CDCl₃) δ 143.2 (C₂Ar), 131.3 (C₆H), 129.6 (C₆H), 119.3 (C₆Br), 28.3 (CH₂CH₃), 15.5 (CH₂CH₃).

ν max (neat) cm⁻¹ 3022, 2963, 2928, 2871, 1485.

Data is in agreement with published data:
Step 2

Supplementary information

2-Methylanisole

\[ \text{KOH (0.54 g, 9.6 mmol) was added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (E)-2-(2-methoxybenzylidene)hydrazine-1-carboxylate (0.50 g, 2.4 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et}_2\text{O (2 × 10 mL). The organic phase was dried (MgSO}_4\text{), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (30% Et}_2\text{O/pentane) to give 2-methylanisole as a yellow oil (0.30 g, 2.5 mmol, quant.).} \]

\[ ^1\text{H NMR (400 MHz, CDCl}_3\text{) δ 7.17–7.11 (2H, m, CH}_2\text{Ar), 6.86–6.79 (2H, m, CH}_2\text{Ar), 3.80 (3H, s, OCH}_3\text{), 2.13 (3H, s, CH}_3\text{).} \]

\[ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{) δ 157.7 (C}_2\text{ArOMe), 130.2 (C}_4\text{ArH), 126.8 (C}_5\text{ArH), 126.6 (C}_6\text{ArH), 120.3 (C}_7\text{ArH), 109.9 (C}_8\text{ArH), 55.2 (OCH}_3\text{), 16.2 (CH}_3\text{).} \]

\[ \nu_{\text{max}} \text{ (neat) cm}^{-1} 2945, 1602, 1591, 1496, 1466, 1243. \]

Data is in agreement with published data:

Diphenylmethane

KOH (0.44 g, 7.9 mmol) was added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl 2-(diphenylmethylene)hydrazine-1-carboxylate (0.50 g, 2.0 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et₂O (2 × 10 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (20% Et₂O/pentane) to give diphenylmethane as a pale yellow oil (0.22 g, 1.3 mmol, 67%).

¹H NMR (400 MHz, CDCl₃) δ 7.26–7.16 (10H, m, CH₆), 3.97 (2H, s, CH₂).

¹³C NMR (100 MHz, CDCl₃) δ 141.2 (C₆), 129.0 (C₆,H), 128.5 (C₆,H), 126.1 (C₆,H), 42.0 (CH₂).

νₘₐₓ (neat) cm⁻¹ 3061, 3026, 2906, 1599, 1493, 1450.

Data is in agreement with published data:

4-Methylanisole

KOH (0.54 g, 9.6 mmol) was added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (E)-2-(4-methoxybenzylidene)hydrazine-1-carboxylate (0.50 g, 2.4 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et₂O (2 × 10 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (30% Et₂O/pentane) to give 4-methylanisole as a pale yellow oil (0.22 g, 1.8 mmol, 76%).

¹H NMR (400 MHz, CDCl₃) δ 7.09 (2H, d, J = 8.6 Hz, CHAr), 6.79 (2H, d, J = 8.6 Hz, CHAr), 3.77 (3H, s, OCH₃), 2.28 (3H, s, CH₃).

¹³C NMR (100 MHz, CDCl₃) δ 157.5 (C₆ArO), 129.9 (C₆H), 129.8 (C₆H), 113.7 (C₆H), 55.3 (OCH₃), 20.4 (CH₃).

ν max (neat) cm⁻¹ 2934, 2834, 1613, 1510, 1464, 1294, 1243.

Data is in agreement with published data:

2-Ethynaphthalene

KOH (0.46 g, 8.3 mmol) was added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (E)-2-(1-(naphthalen-2-yl)ethylidene)hydrazine-1-carboxylate (0.50 g, 2.1 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et₂O (2 × 10 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (5% Et₂O/pentane) to give 2-ethynaphthalene as a pale yellow oil (0.28 g, 1.8 mmol, 86%).

^1H NMR (400 MHz, CDCl₃) δ 7.77–7.71 (3H, m, CH₆), 7.58 (1H, s, CH₆), 7.42–7.34 (2H, m, CH₆), 7.29 (1H, dd, J = 8.4, 1.6 Hz, CH₆), 2.76 (2H, q, J = 7.6 Hz, CH₂CH₃), 1.27 (3H, t, J = 7.6 Hz, CH₂CH₃).

^13C NMR (100 MHz, CDCl₃) δ 140.7 (C₆), 132.6 (C₆), 130.9 (C₆), 126.7 (C₆H), 126.5 (C₆H), 126.4 (C₆H), 126.0 (C₆H), 124.7 (C₆H), 124.5 (C₆H), 123.9 (C₆H), 28.0 (CH₂CH₃), 14.5 (CH₂CH₃).

νmax (neat) cm⁻¹ 2924, 1491, 1090.

Data is in agreement with published data:

4-Chlorotoluene

KOH (0.53 g, 9.4 mmol) was added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (E)-2-(4-chlorobenzylidene)hydrazine-1-carboxylate (0.50 g, 2.4 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et₂O (2 × 10 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (20% Et₂O/pentane) to give 4-chlorotoluene as a pale yellow oil (0.23 g, 1.8 mmol, 76%).

¹H NMR (400 MHz, CDCl₃) δ 7.13 (2H, d, J = 8.4 Hz, C₆H₄), 6.99 (2H, d, J = 8.4 Hz, C₆H₄), 2.22 (3H, s, CH₃).

¹³C NMR (100 MHz, CDCl₃) δ 135.2 (C₆), 130.1 (C₆), 129.3 (C₆,H), 127.2 (C₆,H), 19.8 (CH₃).

νmax (neat) cm⁻¹ 3051, 2964, 2929, 2871, 1601, 1508, 1453.

Data is in agreement with published data:

Step 2

Supplementary information

**4-Methoxydiphenylmethane**

KOH (0.44 g, 7.9 mmol) was added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (E)-2-((4-methoxyphenyl)(phenyl)methylene)hydrazine-1-carboxylate (0.50 g, 2.0 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et<sub>2</sub>O (2 × 10 mL). The organic phase was dried (MgSO<sub>4</sub>), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (30% Et<sub>2</sub>O/pentane) to give 4-methoxydiphenylmethane as a pale yellow oil (0.34 g, 1.7 mmol, 87%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.26–7.24 (2H, m, CH<sub>Ar</sub>), 7.19–7.15 (3H, m, CH<sub>Ar</sub>), 7.08 (2H, d, J = 8.6 Hz, CH<sub>Ar</sub>), 6.83–6.80 (2H, m, CH<sub>Ar</sub>), 3.91 (2H, s, CH<sub>2</sub>), 3.75 (3H, s, OCH<sub>3</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.9 (OCS<sub>H</sub>), 140.5 (CS<sub>Ar</sub>), 132.2 (CS<sub>Ar</sub>), 128.8 (CS<sub>Ar</sub>H), 127.8 (CS<sub>Ar</sub>H), 127.4 (CS<sub>Ar</sub>H), 124.9 (CS<sub>Ar</sub>H), 112.8 (CS<sub>Ar</sub>H), 54.2 (OCH<sub>3</sub>), 40.0 (CH<sub>2</sub>).

ν<sub>max</sub> (neat) cm<sup>−1</sup> 3027, 2906, 2834, 1610, 1510, 1494, 1453, 1246.

Data is in agreement with published data:

4-(Naphthalen-2-yl)butanoic acid

KOH (1.2 g, 21.0 mmol) was taken into triethylene glycol (10 mL) and heated to 100 °C until it dissolved to give a red/orange solution. 4-(2-(methoxycarbonyl)hydrazono)-4-(naphthalen-2-yl)butanoic acid ((1.3 g, 4.2 mmol) was added in one portion and the reaction heated at 140 °C overnight. The reaction was allowed to cool, diluted with water, acidified with 1 M HCl, and the aqueous phase extracted into EtOAc (3 x 20 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (80% EtOAc/40–60 pet. ether) to give 4-(naphthalen-2-yl)butanoic acid as a tan solid (0.62 g, 2.9 mmol, 69%).

¹H NMR (400 MHz, d6-DMSO): δ 12.08 (1H, s, OH), 7.88-7.81 (3H, m, CHAr), 7.68 (1H, s, CHAr), 7.46 (2H, app. quin. d, J = 6.8, 1.4 Hz, CHAr), 7.38 (1H, dd, J = 8.4, 1.4 Hz, CHAr), 2.76 (2H, t, J = 7.4 Hz, CH₂), 2.26 (2H, t, J = 7.4 Hz, CH₂), 1.89 (2H, quin., J = 7.4 Hz, CH₂).

¹³C NMR (100 MHz, d6-DMSO): δ 174.1 (C=O), 139.1 (C₆H), 133.1 (C₆H), 131.5 (C₆H), 127.7 (C₆H), 127.4 (C₆H), 127.2 (C₆H), 126.1 (C₆H), 125.9 (C₆H), 125.1 (C₆H), 34.4 (CH₂), 33.0 (CH₂), 26.0 (CH₂).

υmax (neat) cm⁻¹ 2943, 1685, 1507, 1432m, 1406, 1339, 1271, 1199.

HRMS (−ESI) m/z [(M-H)−found 213.0927 C₁₄H₁₃O₂ requires 213.0921].

m.p. (EtOAc) 98 °C.

Data is in agreement with published data:

2,3-Dimethylthiophene

KOH (0.57 g, 10 mmol) was added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (E)-2-((3-methylthiophen-2-yl)methylene)hydrazine-1-carboxylate (0.50 g, 2.5 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et₂O (2 × 10 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (10% Et₂O/pentane) to give 2,3-dimethylthiophene as a pale yellow oil (217 mg, 2.0 mmol, 77%).

¹H NMR (400 MHz, CDCl₃) δ 6.95 (1H, d, J = 5.1 Hz, CH₁), 6.76 (1H, d, J = 5.1 Hz, CH₂), 2.33 (3H, s, CH₃), 2.13 (3H, s, CH₃).

¹³C NMR (100 MHz, CDCl₃) δ 133.0 (C₆), 132.6 (C₅), 130.0 (C₃,H), 120.6 (C₅,H), 13.6 (CH₃), 13.0 (CH₃).

νmax (neat) cm⁻¹ 2919, 2861, 1438, 1232.

Data is in agreement with published data:

2-Ethylthiophene

KOH (0.57 g, 10 mmol) was added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (E)-2-(1-(thiophen-2-yl)ethylidene)hydrazine-1-carboxylate (0.50 g, 2.5 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et₂O (2 × 10 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (10% Et₂O/pentane) to give 2-ethylthiophene as a pale yellow oil (0.22 g, 2.0 mmol, 77%).

Product contains a trace of the corresponding azine (<5%). Only major peaks reported.

$^1$H NMR (400 MHz, CDCl₃) δ 7.06 (1H, dd, J = 5.1, 1.2 Hz, CH₆H), 6.91 (1H, dd, J = 5.1, 3.4 Hz, CH₆H), 6.78 (1H, dd, J = 3.4, 1.1 Hz, CH₆H), 3.91 (2H, q, J = 7.5 Hz, CH₂CH₃), 1.31 (3H, t, J = 7.5 Hz, CH₂CH₃).

$^{13}$C NMR (100 MHz, CDCl₃) δ 147.5 (C₆C), 126.7 (C₆H), 123.3 (C₆H), 122.7 (C₆H), 23.3 (CH₂CH₃), 16.1 (CH₂CH₃).

ν_{max} (neat) cm⁻¹: 3073, 2966, 2926, 2852, 1591, 1429, 1363, 1290.

Data is in agreement with published data:

**3-Ethylpyridine**

KOH (0.58 g, 10 mmol) was added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (E)-2-(1-(pyridin-3-yl)ethylidene)hydrazine-1-carboxylate (0.50 g, 2.6 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et₂O (2 × 10 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (40% Et₂O/pentane) to give 3-ethylpyridine as a pale yellow oil (0.21 g, 2.0 mmol, 76%).

¹H NMR (400 MHz, CDCl₃): δ 8.36 (1H, d, J = 1.5 Hz, CH₂), 8.32 (1H, d, J = 7.8 Hz, CH₂), 7.38 (1H, d, J = 7.8 Hz, CH₂), 7.08 (1H, dd, J = 7.8, 7.8 Hz, CH₂), 2.53 (2H, q, J = 7.6 Hz, CH₂), 1.14 (3H, t, J = 7.6 Hz, CH₃).

¹³C NMR (100 MHz, CDCl₃): δ 148.5 (C₆H), 146.2 (C₆H), 138.2 (C₆H), 134.2 (C₆H), 122.2 (C₆H), 25.0 (CH₂CH₂), 14.3 (CH₂CH₂).

ν max (neat) cm⁻¹: 3500, 2967, 2932, 1575, 1478, 1422.

Data is in agreement with published data:

2-Ethyl-5-methylfuran

KOH (0.57 g, 10 mmol) was added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (E)-2-(1-(5-methylfuran-2-yl)ethylidene)hydrazine-1-carboxylate (0.50 g, 2.6 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et₂O (2 × 10 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (40% Et₂O/pentane) to give 2-ethyl-5-methylfuran as an extremely volatile pale yellow oil (0.20 g, 1.8 mmol, 69%).

Removal of some of the volatile product revealed the presence of trace quantities of azine. Only the product peaks are reported.

¹H NMR (400 MHz, CDCl₃) δ 5.76 (2H, s, CH₂), 2.53 (2H, q, J = 7.5 Hz, CH₂CH₃), 2.17 (3H, s, CH₃), 1.13 (3H, t, J = 7.6 Hz, CH₂CH₃).

¹³C NMR (100 MHz, CDCl₃) δ 155.0 (C₆), 149.0 (C₆H), 104.7 (C₆H), 103.3 (C₆H), 20.3 (CH₂CH₃), 12.4 (CH₃), 11.3 (CH₂CH₃).

νmax (neat) cm⁻¹ 2973, 2924, 1742, 1570, 1521, 1453, 1372.

Data is in agreement with published data:

**Isobutylbenzene**

KOH (0.51 g, 9.1 mmol) was added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (E)-2-(2-methyl-1-phenylpropylidene)hydrazine-1-carboxylate (0.50 g, 2.3 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et₂O (2 × 10 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography (10% Et₂O/pentane) to give isobutylbenzene as a pale yellow oil (0.16 g, 1.2 mmol, 53%) that was contaminated with 30% of the corresponding azine as an inseparable mixture.

Only peaks the desired product are reported.

**¹H NMR (400 MHz, CDCl₃)** \( \delta 7.26–7.06 \) (5H, m, \( CH_Ar \)), 2.41 (2H, d, \( J = 7.2 \) Hz, \( CH_2 \)), 1.83–1.76 (1H, m, \( CH(CH_3)_2 \)), 0.83 (6H, d, \( J = 6.6 \) Hz, \( CH(CH_3)_2 \)).

**¹³C NMR (100 MHz, CDCl₃)** \( \delta 140.7 \) (\( C_Ar \)), 127.6 (\( C_Ar H \)), 127.0 (\( C_Ar H \)), 124.6 (\( C_Ar H \)), 45.3 (\( CH_2 \)), 30.6 (\( CH(CH_3)_2 \)), 22.6 (\( CH(CH_3)_2 \)).

\( \nu_{max} \) (neat) cm⁻¹ 3027, 2906, 2834, 1610, 1510, 1494, 1453, 1246.

Data is in agreement with published data:

2-(2-(2-(p-tolyloxy)ethoxy)ethoxy)ethan-1-ol

\[
\text{\begin{center}
\begin{tikzpicture}
\node (A) at (0,0) {\includegraphics[width=0.5\textwidth]{structure.png}};
\end{tikzpicture}
\end{center}
}\]

KOH (0.57 g, 10 mmol) was added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (\(E\))-2-(4-fluorobenzylidene)hydrazine-1-carboxylate (0.50 g, 2.6 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et\(_2\)O (3 \times 10 mL). The organic phase was dried (MgSO\(_4\)), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (30% Et\(_2\)O/pentane) to give 2-(2-(2-(p-tolyloxy)ethoxy)ethoxy)ethan-1-ol as a pale yellow oil (0.26 g, 1.1 mmol, 41%).

\(\begin{align*}
\text{\(^1\)H NMR (400 MHz, CDCl}_3\)} & \delta 7.96 (2H, \text{d, } J = 8.4 \text{ Hz, } \text{C}_\text{Ar} \text{O}), 6.72 (2H, \text{d, } J = 8.4 \text{ Hz, } \text{C}_\text{Ar}), 4.02–3.97 (2\text{H, m, OCH}_2), 3.74–3.72 (2\text{H, m, OCH}_2), 3.66–3.50 (6\text{H, m, OCH}_3), 3.50–3.48 (2\text{H, m, OCH}_3), 3.01 (1\text{H, br s, OH}), 2.16 (3\text{H, s, CH}_3).
\end{align*}\)

\(\begin{align*}
\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\)} & \delta 155.6 (\text{C}_{\text{Ar}} \text{O}), 129.0 (\text{C}_{\text{Ar}}), 128.8 (\text{C}_{\text{Ar}} \text{H}), 113.4 (\text{C}_{\text{Ar}} \text{H}), 71.6 (\text{OCH}_3), 69.3 (\text{OCH}_3), 68.7 (\text{OCH}_3), 66.4 (\text{OCH}_3), 60.6 (\text{OCH}_3), 19.4 (\text{CH}_3).
\end{align*}\)

\(\nu\text{max (neat) cm}^{-1} 3429, 2870, 1613, 1510, 1455, 1241.\)

HRMS (+ESI) \(m/z\) ([M+Na]\(^{+}\) found 263.1254 \(\text{C}_{13}\text{H}_{20}\text{O}_4\text{Na}\) requires 263.1254].
KOH (0.45 g, 8.0 mmol) was added to triethylene glycol (5.0 mL) and heated to 100 °C until it dissolved to give a red/orange solution. Methyl (E)-2-(3,5-di-tert-butyl-2-hydroxybenzylidene)hydrazine-1-carboxylate (0.50 g, 1.6 mmol) was added in one portion and the reaction heated at 140 °C for 4 hours. The reaction was allowed to cool, diluted with water and the aqueous phase extracted into Et₂O (3 x 10 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography (20% EtOAc/40–60 pet. ether) to give 6,6'-(1E,1'E)-hydrazine-1,2-diylidenebis(methanlylidene))bis(2,4-di-tert-butylphenol) as a pale yellow solid (0.27 g, 1.2 mmol, 76%).

¹H NMR (400 MHz, CDCl₃) 8 11.89 (2H, s, OH), 8.76 (2H, s, HCN=N), 7.45 (2H, d, J = 2.4 Hz, CH₃CH₂), 7.16 (2H, d, J = 2.4 Hz, CH₃CH₂), 1.47 (18H, s, C(CH₃)₃), 1.32 (18H, s, C(CH₃)₃).

¹³C NMR (100 MHz, CDCl₃) 8 164.4 (C=N), 156.9 (C₆O), 141.4 (C₅H₅Bu), 137.0 (C₅H₅Bu), 128.3 (C₆H), 127.0 (C₅H), 116.7 (C₆H), 35.2 (C(CH₃)₃), 34.2 (C(CH₃)₃), 31.5 (C(CH₃)₃), 29.5 (C(CH₃)₃).

ν_max (neat) cm⁻¹ 2957, 2869, 1622, 1591, 1456, 1436.

HRMS (+ESI) m/z [(M+H)⁺] found 465.3476 C₃₀H₄₅N₂O₂ requires 465.3476.

m.p. (EtOAc/pet. ether) 208–210 °C
Additional Procedures

Preparation of 4-(Naphthalen-2-yl)-4-oxobutanoic acid

![Chemical Structure](image)

Naphthalene (5.0 g, 39 mmol) and succinic anhydride (3.9 g, 39 mmol) were dissolved in nitro benzene (100 mL). AlCl$_3$ (10.4 g, 78 mmol) was added in four portions, which led to warming of the mixture. The reaction was stirred at ambient temperature for 18 hours before being poured on ice, acidified with 100 mL 2 M HCl and vigorously stirred for 30 minutes to break up the brown suspension. The mixture was filtered and the solid was washed with H$_2$O (2 x 50 mL) and hexane (2 x 50 mL). To remove residual alpha-substituted impurities the brown solid was suspended in toluene (75 mL) and heated at 100 °C for 15 minutes before being allowed to cool to ambient temperature overnight. The suspension was filtered and dried in a vacuum oven to give 4-(naphthalen-2-yl)-4-oxobutanoic acid as a tan solid (3.3 g, 14 mmol, 37%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.52 (1H, s, CH$_{Ar}$), 8.05 (1H, dd, $J = 8.6, 1.8$ Hz, CH$_{Ar}$), 7.98 (1H, d, $J = 8.2$, CH$_{Ar}$), 7.93 – 7.87 (2H, m, CH$_{Ar}$), 7.64 – 7.54 (2H, m, CH$_{Ar}$), 3.49 (2H, t, $J = 6.6$, CH$_2$), 2.89 (2H, t, $J = 6.6$, CH$_2$).

$^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ 198.4 (C=O), 173.8 (C=O), 135.0 (C$_{Ar}$), 133.7 (C$_{Ar}$), 132.2 (C$_{Ar}$), 129.8 (C$_{Ar}$), 129.6 (C$_{Ar}$), 128.6 (C$_{Ar}$), 128.2 (C$_{Ar}$), 127.6 (C$_{Ar}$), 126.9 (C$_{Ar}$), 123.4 (C$_{Ar}$), 33.1 (CH$_2$), 28.0 (CH$_2$).

IR (neat, cm$^{-1}$): 3200 br, 1709, 1677, 1592, 1465, 1399, 1370, 1315, 1251, 1230, 1169, 1126, 935, 809.

HRMS (–ESI) m/z [(M-H) – found 227.0719 C$_{14}$H$_{11}$O$_3$ requires 227.0714].

m.p. (Toluene) 172 °C.

Data is in agreement with published data: