Supporting Information

Three-Component Azidation of Styrene-Type Double Bonds: Light-Switchable Behavior of a Copper Photoredox Catalyst**

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Supporting Information
1 General information

$^1$H-NMR, $^{13}$C($^1$H)-NMR and $^{19}$F-NMR were recorded at 500/400 MHz, 125/100 MHz, 470/376 MHz on a Bruker Avance 500 or 400 spectrometers. All spectra are referenced to CDCl$_3$ residual CHCl$_3$ peak ($^1$H-NMR $\delta$ = 7.26 ppm; $^{13}$C($^1$H)-NMR $\delta$ = 77.0 ppm). All chemical shifts are quoted in parts per million (ppm), measured from the centre of the signal except in the case of multiplets of more than one proton, which are quoted as a range. Coupling constants are quoted to the nearest 0.1 Hz. Splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin.), heptet (hept.), multiplet (m), broad singlet (brs) and combinations thereof.

Infrared spectra were recorded on a spectrometer as neat using a Perkin-Elmer FT-IR Spectrum RX1 or BX spectrometers.

LCMS analysis was performed on a Agilent 1200 series fitted with a 3.0 x 20 mm, C18, 3.0 $\mu$m column, with a single quadrupole Agilent 6100 mass spectrometrer, with ESI ionisation. Elution was carried out using reverse phase gradient of MeOH-water with 0.1% formic acid.

Low resolution mass spectrometry was performed on an Agilent 6100 mass spectrometer (ESI ionisation) and Hewlett Packard 5971 MSD (GC/MS with EI). High resolution mass spectrometry was performed on a Waters QTOF with ESI/APCI ionisation and a Thermo Finnigan MAT95XP (EI).

Melting points were determined using a Kofler hot-stage apparatus or Stuart Scientific SMP10 apparatus and are uncorrected. Thin layer chromatography (TLC) was performed using pre-coated Merck 60F254 silica plates. Visualization was performed using either UV light or treatment with acidic potassium permanganate. Flash chromatography was performed using Merck Kieselgel (mesh size 220-240) silica.

All reagents and solvents were used as obtained from commercial source, unless otherwise stated. Solvents were degassed by bubbling nitrogen gas through them for twenty minutes prior to use.

1-azido-1,3-benzo[d][1,2]iodaoxol-3(1H)-one,$^1$ 2-vinylbenzofuran,$^2$ Cu(dap)$_2$Cl,$^3$ 2-vinylthiophene$^4$ and 2-(prop-2-yn-1-yloxy)styrene$^5$ were synthesised according to literature procedures.

Safety: Azides are potentially explosive compounds and require appropriate safety protocols to be observed at all times.$^6$

N.B. Whilst 1-Azido-1,3-benzo[d][1,2]iodaoxol-3(1H)-one, 1, is more stable than other iodine azide reagents, it is reported to decompose with explosion at 138-139°C.$^7$ In the course of reaction optimisation for this work, we observed an explosive decomposition of reagent 1 (100 mg, (s)) in the presence of excess KSCN (s) in a vial at room temperature.
2 Optimisation screenings

2.1 Catalyst screening

A vial containing the photoredox catalyst (5 µmol, 0.01 eq), 1-azido-1,3-benzo[d][1,2]iodaoxol-3(1H)-one (145 mg, 0.5 mmol, 1 eq) and equipped with a stirrer bar, sealed with a septum, was purged under a flux of nitrogen. Then degassed methanol (5 mL) and styrene (290 µL, 2.5 mmol, 5 eq) were added and the tube was sealed and put 1 cm away from a 30 W fluorescent bulb and stirred for 18 hours. The reaction mixture was loaded on silica and purified by flash column chromatography eluting with a mixture hexane:ethyl acetate = 100:0 to 95:5.

Table 1: * Isolated yields.

| Entry | Catalyst                          | Yield* |
|-------|----------------------------------|--------|
| 1     | Ir(ppy)_3                        | dcmp – trace of product |
| 2     | Ir(dtbbpy)(ppy)_2PF_6             | -      |
| 3     | Ru(bpy)_3Cl_2                    | -      |
| 4     | Eosin Y                          | -      |
| 5     | Methylene Blue                   | -      |
| 6     | Fluorescein                      | -      |
| 7     | Rhodamine 6G                     | -      |
| 8     | Rose Bengal                      | -      |
| 9     | Acridinium 2                     | traces |
| 10    | Cu(dap)_2Cl                      | 60%    |

S3
2.2 Additive Screening

| Entry | Additive     | Yield<sup>a</sup> |
|-------|--------------|-------------------|
| 1     | Zn(OAc)<sub>2</sub> | 44%               |
| 2     | KOAc         | < 5%              |
| 3     | Ni(OAc)<sub>2</sub> | < 5%             |
| 4     | Co(OAc)<sub>2</sub> | < 5%             |
| 5     | K<sub>2</sub>CO<sub>3</sub> | < 5%             |
| 6     | ZnCO<sub>3</sub> | < 5%              |
| 7     | Ti(O<sub>i</sub>Pr)<sub>4</sub> | < 5%             |
| 8     | Ag(O<sub>2</sub>CCF<sub>3</sub>) | < 5%             |
| 9     | Mn(OAc)<sub>3</sub> | 50%              |
| 10    | FeSO<sub>4</sub> | 58%              |
| 11    | Zn(ClO<sub>4</sub>)<sub>2</sub> | 50%             |

Table 2: <sup>a</sup> Isolated yields.

A vial containing Cu(dap)<sub>2</sub>Cl (4.4 mg, 5 μmol, 0.01 eq), 1-azido-1-λ<sup>3</sup>-benzo[d][1,2]iodaoxol-3(1H)-one (145 mg, 0.5 mmol, 1 eq), the additive and equipped with a stirrer bar, sealed with a septum, was purged under a flux of nitrogen. Then degassed methanol (5 mL) and styrene (290 μL, 2.5 mmol, 5 eq) were added and the tube was sealed and put 1 cm away from a 30 W fluorescent bulb and stirred for 18 hours. The reaction mixture was loaded on silica and purified by flash column chromatography eluting with a mixture hexane:ethyl acetate = 100:0 to 95:5.
2.3 Stoichiometry assessment

\[
\begin{align*}
\text{2a} & \quad + \quad \text{Cu(dap)}_2\text{Cl} (x \text{ mol\%}) \\
\text{MeOH, 30 W light bulb} & \quad \text{18 h, r.t.} \\
\rightarrow \quad \text{3a}
\end{align*}
\]

| Entry | Eq 1a | Eq 2a | X       | Yield$^a$ |
|-------|-------|-------|---------|-----------|
| 1     | 5     | 1     | 1 mol%  | 60%       |
| 2     | 2     | 1     | 1 mol%  | 36%       |
| 3     | 10    | 1     | 1 mol%  | 58%       |
| 4     | 5     | 1     | 0.5 mol%| 30%       |
| 5     | 5     | 1     | 2 mol%  | 59%       |

Table 3: Conditions: 1eq. = 0.5 mmol. $^a$Isolated yields.

A vial containing Cu(dap)$_2$Cl, 1-azido-1$\alpha^3$-benzo[d][1,2]iodaoxol-3(1H)-one (145 mg, 0.5 mmol, 1 eq) and equipped with a stirrer bar, sealed with a septum, was purged under a flux of nitrogen. Then degassed methanol (5 mL) and styrene (290 $\mu$L, 2.5 mmol, 5 eq) were added and the tube was sealed and put 1 cm away from a 30 W fluorescent bulb and stirred for 18 hours. The reaction mixture was loaded on silica and purified by flash column chromatography eluting with a mixture hexane:ethyl acetate = 100:0 to 95:5.
### A) Methoxyazidation control reactions

![Chemical structure](image)

| Entry | Cu(dap)₂Cl | Light bulb | Yield<sup>a</sup> |
|-------|------------|------------|------------------|
| 1     | Y          | Y          | 61%<sup>b</sup>  |
| 2<sup>c,e</sup> | Y          | N          | 8%               |
| 3     | N          | Y          | -                |
| 4<sup>d</sup> | Y          | Y          | -                |
| 5<sup>f</sup> | N          | Y          | -                |

<sup>a</sup> Isolated yield.  
<sup>b</sup> Yield is the average of 5 reactions.  
<sup>c</sup> <sup>1</sup>H NMR yield.  
<sup>d</sup> Non-degassed methanol was used to perform the reaction.  
<sup>e</sup> Diazidated product was isolated in 94% yield.  
<sup>f</sup> Cu(acac)₂ was used instead of the photoredox catalyst.

Table 4: A vial containing Cu(dap)₂Cl (4.4 mg, 5 μmol, 0.01 eq), 1-azido-1,3-benzo[d][1,2]iodaoxol-3(1H)-one (145 mg, 0.5 mmol, 1 eq) and equipped with a stirrer bar, sealed with a septum, was purged under a flux of nitrogen. Then degassed methanol (5 mL) and styrene (290 μL, 2.5 mmol, 5 eq) were added and the tube was sealed and put 1 cm away from a 30 W fluorescent bulb and stirred for 18 hours. The reaction mixture was loaded on silica and purified by flash column chromatography eluting with a mixture hexane:ethyl acetate = 100:0 to 95:5.

### B) Diazidation control reaction

![Chemical structure](image)

| Entry | CuX | Yield<sup>a</sup> |
|-------|-----|------------------|
| 1     | Cu(dap)₂Cl | 94%             |
| 2<sup>b</sup> | Cu(acac)₂ | < 80%           |
| 3<sup>b</sup> | CuCl | < 80%           |
| 4<sup>b,c</sup> | CuCl | < 80%           |

<sup>a</sup> Isolated yield.  
<sup>b</sup> The reaction yields a complex mixture containing the product other unknown compounds. Based on the mass of the sample retrieved after column chromatography, we can quote a yield range.  
<sup>c</sup> Reaction performed under visible light irradiation with a 30 W light bulb.

Table 5: A vial containing Cu(dap)₂Cl (4.4 mg, 5 μmol, 0.01 eq), 1-azido-1,3-benzo[d][1,2]iodaoxol-3(1H)-one (145 mg, 0.5 mmol, 1 eq) and equipped with a stirrer bar, sealed with a septum, was purged...
under a flux of nitrogen. Then degassed methanol (5 mL) and styrene (290 μL, 2.5 mmol, 5 eq) were added in the dark and the tube was sealed and stirred for 18 hours. The reaction mixture was loaded on silica and purified by flash column chromatography eluting with a mixture hexane:ethyl acetate = 100:0 to 98:2.

A vial containing Cu(dap)_2Cl (4.4 mg, 5 μmol, 0.01 eq), 1,2-diazidoethylbenzene (X mg, X mmol, 1 eq) and equipped with a stirrer bar, sealed with a septum, was purged under a flux of nitrogen. Then degassed methanol (5 mL) and styrene (290 μL, 2.5 mmol, 5 eq) were added and the tube was sealed and put 1 cm away from a 30 W fluorescent bulb and stirred for 18 hours. The reaction mixture was loaded on silica and purified by flash column chromatography eluting with a mixture hexane:ethyl acetate = 100:0 to 98:2.

C) TEMPO control reaction

A vial containing Cu(dap)_2Cl (4.4 mg, 5 μmol, 0.01 eq), 1-azido-1,λ^3-benzo[d][1,2]iodaoxol-3(1H)-one (145 mg, 0.5 mmol, 1 eq) and equipped with a stirrer bar, sealed with a septum, was purged under a flux of nitrogen. Then a solution of TEMPO (156 mg, 1 mmol, 2 eq) in degassed methanol (5 mL) and styrene (290 μL, 2.5 mmol, 5 eq) were added and the tube was sealed and put 1 cm away from a 30 W fluorescent bulb and stirred for 18 hours.
2.5 Time-Control Experiments

\[
\begin{align*}
\text{ Cresol (2a)} + \text{ Cu(dap)}_2\text{Cl} (1 \text{ mol}) \\
\text{MeOH, 30 W light bulb} \\
x \text{ h, r.t.} \\
\rightarrow \text{ 3a}
\end{align*}
\]

| Entry | Eq 1a | Eq 2a | Time | Yield \(^a\) |
|-------|-------|-------|------|-------------|
| 1     | 5     | 1     | 0.5 h| 27%         |
| 2     | 5     | 1     | 1 h  | 45%         |
| 3     | 5     | 1     | 2 h  | 46%         |
| 4     | 5     | 1     | 3 h  | 50%         |
| 5     | 5     | 1     | 5 h  | 54%         |
| 6     | 5     | 1     | 18 h | 60%         |

Table 5: \(^a\) Isolated yield

A vial containing Cu(dap)\(_2\)Cl (4.4 mg, 5 \(\mu\)mol, 0.01 eq), 1-azido-1\(\lambda^3\)-benzo[d][1,2]iodaoxol-3(1H)-one (145 mg, 0.5 mmol, 1 eq) and equipped with a stirrer bar, sealed with a septum, was purged under a flux of nitrogen. Then degassed methanol (5 mL) and styrene (290 \(\mu\)L, 2.5 mmol, 5 eq) were added and the tube was sealed and put 1 cm away from a 30 W fluorescent bulb and stirred for a certain number of hours. The reaction mixture was loaded on silica and purified by flash column chromatography eluting with a mixture hexane:ethyl acetate = 100:0 to 95:5.
2.6 Nucleophiles addition

![Chemical structure](image)

| Entry | Nu   | Eq Nu | Yield$^a$ |
|-------|------|-------|-----------|
| 1     | NaN₃ | 5     | 70%       |
| 2     | NaN₃ | 10    | 96%       |
| 3     | NaBr | 10    | 46%       |
| 4     | LiBr | 10    | < 5%      |
| 5     | KBr  | 10    | < 5%      |
| 6     | TBAB | 10    | nr        |

Table 5: $^a$Isolated yield

A vial containing Cu(dap)$_2$Cl (4.4 mg, 5 μmol, 0.01 eq), 1-azido-1,2,3-benzo[2,3][1,2]iodaioxol-3(1H)-one (145 mg, 0.5 mmol, 1 eq), a suitable nucleophile and equipped with a stirrer bar, sealed with a septum, was purged under a flux of nitrogen. Then degassed acetonitrile (5 mL) and styrene (290 μL, 2.5 mmol, 5 eq) were added and the tube was sealed and put 1 cm away from a 30 W fluorescent bulb and stirred for a certain number of hours. The reaction mixture was loaded on silica and purified by flash column chromatography eluting with a mixture hexane:ethyl acetate = 100:0 to 95:5.
3 Typical procedures for the three component azido-functionalisation of styrenes

General procedure A
A vial containing Cu(dap)\textsubscript{2}Cl (4.4 mg, 5 \(\mu\)mol, 0.01 eq), 1-azido-1\(\lambda^3\)-benzo[\(d\)][1,2]iodaoxol-3(1\(H\))-one (145 mg, 0.5 mmol, 1 eq) and equipped with a stirrer bar, sealed with a septum, was purged under a flux of nitrogen. Then degassed methanol (5 mL) and the styrene (2.5 mmol, 5 eq) were added and the tube was sealed and put 1 cm away from a 30 W fluorescent bulb and stirred for 18 hours. The reaction mixture was loaded on silica and purified by flash column chromatography eluting with a mixture hexane:ethyl acetate = 100:0 to 95:5.

General procedure B (for the trapping of different solvents)
A vial containing Cu(dap)\textsubscript{2}Cl (4.4 mg, 5 \(\mu\)mol, 0.01 eq), 1-azido-1\(\lambda^3\)-benzo[\(d\)][1,2]iodaoxol-3(1\(H\))-one (145 mg, 0.5 mmol, 1 eq) and equipped with a stirrer bar, sealed with a septum, was purged under a flux of nitrogen. Then degassed solvent (5 mL) and the styrene (2.5 mmol, 5 eq) were added and the tube was sealed and put 1 cm away from a 30 W fluorescent bulb and stirred for 18 hours. The reaction mixture was loaded on silica and purified by flash column chromatography eluting with a mixture hexane:ethyl acetate = 100:0 to 95:5.

General procedure C (for the trapping of different nucleophiles)
A vial containing Cu(dap)\textsubscript{2}Cl (4.4 mg, 5 \(\mu\)mol, 0.01 eq), 1-azido-1\(\lambda^3\)-benzo[\(d\)][1,2]iodaoxol-3(1\(H\))-one (145 mg, 0.5 mmol, 1 eq), the nucleophile (5 mmol, 10 eq) and equipped with a stirrer bar, sealed with a septum, was purged under a flux of nitrogen. Then degassed acetonitrile (5 mL) and the styrene (2.5 mmol, 5 eq) were added and the tube was sealed and put 1 cm away from a 30 W fluorescent bulb and stirred for 18 hours. The reaction mixture was loaded on silica and purified by flash column chromatography eluting with a mixture hexane:ethyl acetate = 100:0 to 95:5.

General procedure D (for the diazidation)
A vial containing Cu(dap)\textsubscript{2}Cl (4.4 mg, 5 \(\mu\)mol, 0.01 eq), 1-azido-1\(\lambda^3\)-benzo[\(d\)][1,2]iodaoxol-3(1\(H\))-one (145 mg, 0.5 mmol, 1 eq) and equipped with a stirrer bar, sealed with a septum, was covered in aluminium foil and purged under a flux of nitrogen. Then degassed methanol (5 mL) and the styrene (2.5 mmol, 5 eq) were added and the tube was sealed the reaction mixture stirred for 18 hours in the dark. The reaction mixture was loaded on silica and purified by flash column chromatography eluting with a mixture hexane:ethyl acetate = 100:0 to 98:2.
4 Characterisation data for methoxyazidated compounds 3a – s and oxazocine

(2-azido-1-methoxyethyl)benzene (3a)

Prepared according to general procedure A reacting styrene (290 µL). The title compound was obtained as a colourless oil (53 mg, 60%). Data are in accordance with previous literature reports.\(^8\)

\(^{1}\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.44 – 7.36 (m, 2H), 7.37 – 7.30 (m, 3H), 4.36 (dd, \(J\) = 8.5, 3.6 Hz, 1H), 3.49 (dd, \(J\) = 13.0, 8.5 Hz, 1H), 3.32 (s, 3H), 3.21 (dd, \(J\) = 13.0, 3.6 Hz, 1H).

\(^{13}\)C NMR (125 MHz, Chloroform-\(d\)) \(\delta\) 138.5, 128.8, 128.5, 126.7, 83.2, 57.0, 56.6. IR (neat film): 2927, 2096, 1453, 1107, 700. MS (EI): 177 (M – \(\text{N}_2\), 0.9), 121 (M – \(\text{CH}_2\text{N}_3\), 100). HRMS (EI): Calculated for C\(_9\)H\(_{11}\)NO (M – \(\text{N}_2\)): 149.0835; Found: 149.0832.

1-(2-azido-1-methoxyethyl)-2-methylbenzene (3b)

Prepared according to general procedure A reacting 2-methylstyrene (330 µL). The title compound was obtained as a colourless oil (53 mg, 55%). \(^{1}\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.40 (dd, \(J\) = 7.4, 1.7 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.22 (td, \(J\) = 7.2, 1.7 Hz, 1H), 7.18 – 7.13 (m, 1H), 4.64 (dd, \(J\) = 8.8, 3.2 Hz, 1H), 3.44 (dd, \(J\) = 13.2, 8.8 Hz, 1H), 3.30 (s, 3H), 3.15 (dd, \(J\) = 13.2, 3.2 Hz, 1H), 2.33 (s, 3H).

\(^{13}\)C NMR (125 MHz, Chloroform-\(d\)) \(\delta\) 136.4, 135.5, 130.7, 128.0, 126.5, 126.0, 79.9, 56.9, 55.6, 19.0. IR (neat film): 2925, 2099, 1460, 1104, 757. MS (EI): 163 (M – \(\text{N}_2\), 2), 135 (M – \(\text{CH}_2\text{N}_3\), 100). HRMS (EI): Calculated for C\(_9\)H\(_{11}\)O (M – \(\text{CH}_2\text{N}_3\)): 135.0804; Found: 135.0807.

1-(2-azido-1-methoxyethyl)-3-methylbenzene (3c)

Prepared according to general procedure A reacting 3-methylstyrene (340 µL). The title compound was obtained as a colourless oil (73 mg, 76%). \(^{1}\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.31 – 7.24 (m, 1H), 7.19 – 7.06 (m, 3H), 4.32 (dd, \(J\) = 8.8, 3.5 Hz, 1H), 3.48 (dd, \(J\) = 13.0, 8.8 Hz, 1H), 3.31 (s, 3H), 3.19 (dd, \(J\) = 13.0, 3.5 Hz, 1H), 2.37 (s, 3H).

\(^{13}\)C NMR (125 MHz, Chloroform-\(d\)) \(\delta\) 138.5, 138.4, 129.2, 128.6, 127.3, 123.8, 83.2, 56.9, 56.6, 21.5. IR (neat film): 2924, 2097, 1453, 1111, 704. MS (EI): 163 (M – \(\text{N}_2\), 4), 135 (M – \(\text{CH}_2\text{N}_3\), 100). HRMS (EI): Calculated for C\(_9\)H\(_{11}\)O (M – \(\text{CH}_2\text{N}_3\)): 135.0804; Found: 135.0807.
1-(2-azido-1-methoxyethyl)-4-methylbenzene (3d)

Prepared according to general procedure A reacting 4-methylstyrene (330 µL). The title compound was obtained as a colourless oil (60 mg, 63%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.20 (s, 4H), 4.33 (dd, $J = 8.6$, 3.6 Hz, 1H), 3.48 (dd, $J = 13.0$, 8.6 Hz, 1H), 3.30 (s, 3H), 3.19 (dd, $J = 13.0$, 3.6 Hz, 1H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 138.2, 135.5, 129.4, 126.6, 83.0, 56.8, 56.6, 21.2. IR (neat film): 2925, 2094, 1448, 1253, 1107, 813. MS (EI): 163 (M - N$_2$, 3), 135 (M - CH$_2$N$_3$, 100). HRMS (APCI): Calculated for C$_{10}$H$_{14}$NO (M + H$^+$ - N$_2$): 164.1075; Found: 164.1074.

1-(2-azido-1-methoxyethyl)-2,4,6-trimethylbenzene (3e)

Prepared according to general procedure A reacting 2,4,6-trimethylstyrene (403 µL). The title compound was obtained as a colourless oil (97 mg, 89%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 6.84 (s, 2H), 4.85 (dd, $J = 9.6$, 3.8 Hz, 1H), 3.76 (dd, $J = 13.1$, 9.6 Hz, 1H), 3.26 (s, 3H), 3.15 (dd, $J = 13.1$, 3.8 Hz, 1H), 2.37 (s, 6H), 2.26 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 137.5, 136.9, 130.4, 130.3 (broad signal), 80.2, 56.4, 53.7, 20.8, 20.5 (broad signal). IR (neat film): 2926, 2095, 1449, 1253, 1110, 850. MS (EI): 191 (M - N$_2$, 20), 163 (M - CH$_2$N$_3$, 100). HRMS (APCI): Calculated for C$_{12}$H$_{18}$NO (M + H$^+$ - N$_2$): 192.1359; Found: 192.1394.

2-(2-azido-1-methoxyethyl)naphthalene (3f)

Prepared according to general procedure A reacting 2-vinylnapthalene (385 mg). The title compound was obtained as a yellow oil (110 mg, 70 %). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.90 – 7.82 (m, 3H), 7.79 (s, 1H), 7.56 – 7.47 (m, 2H), 7.44 (dd, $J = 8.4$, 1.9 Hz, 1H), 4.54 (dd, $J = 8.5$, 3.6 Hz, 1H), 3.59 (dd, $J = 13.0$, 8.5 Hz, 1H), 3.36 (s, 3H), 3.30 (dd, $J = 13.0$, 3.6 Hz, 1H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 136.0, 133.4, 133.2, 128.7, 127.9, 127.8, 126.4, 126.3, 126.2, 124.1, 83.3, 57.1, 56.6. IR (neat film): 3056, 2926, 2097, 1442, 1255, 1106, 810, 745. MS (ESI): 250 (M + Na$^+$). HRMS (APCI): Calculated for C$_{13}$H$_{14}$NO (M + H$^+$ - N$_2$): 200.1075; Found: 200.1064.

2-azido-1-methoxy-2,3-dihydro-1H-indene (3g)

Prepared according to general procedure A reacting indene (292 µL). The title compound was obtained as a colourless oil (54 mg, 56%), contaminated with small amounts of the diazide 4a. Trans-diastereomer: $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.38 (dd, $J = 7.1$, 1.6 Hz, 1H), 7.33 – 7.15
(m, 3H), 4.71 (d, \( J = 4.7 \) Hz, 1H), 4.17 (ddd, \( J = 7.4, 6.0, 4.7 \) Hz, 1H), 3.58 (s, 3H), 3.37 (dd, \( J = 16.1, 7.4 \) Hz, 1H), 2.90 (dd, \( J = 16.1, 6.0 \) Hz, 1H). \(^{13}\)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 139.9, 139.3, 129.1, 127.3, 125.1, 125.0, 88.5, 66.9, 57.7, 35.9. IR (neat film, significant peaks): 2926, 2097, 1461, 1259, 1093, 747. MS (ESI): 212 (M + Na\(^{+}\)). HRMS (APCI): Calculated for C\(_{10}\)H\(_{12}\)NO (M + H\(^{+}\) - N\(_2\)): 162.0919; Found: 162.0921.

2-azido-1-methoxy-1,2,3,4-tetrahydronaphthalene (3h)

Prepared according to general procedure A reacting 1,2-dihydronaphthalene (326 \( \mu \)L). The two diastereomers of the title compound were obtained as colourless oils (53 mg, \textit{cis}:\textit{trans} = 1.4:1, 52%). IR (neat film, significant peaks): 2933, 2091, 1454, 1253, 1081, 746. MS (EI): 175 (M - N\(_2\), 50), 160 (M - HN\(_3\), 100), 132 (M - C\(_2\)H\(_4\)N\(_3\), 90). HRMS (APCI): Calculated for C\(_{11}\)H\(_{14}\)NO (M + H\(^{+}\) - N\(_2\)): 176.1081; Found: 176.1075.

\textbf{Cis-diastereomer (major):} \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.38 (dd, \( J = 5.3, 3.8 \) Hz, 1H), 7.29 – 7.18 (m, 2H), 7.13 – 7.10 (m, 1H), 4.29 (d, \( J_{eq-ax} = 6.4 \) Hz, 1H), 3.96 (ddd, \( J = 8.5, 6.4, 3.4 \) Hz, 1H), 3.56 (s, 3H), 3.06 (ddd, \( J = 17.3, 6.3, 4.7 \) Hz, 1H), 2.95 – 2.78 (m, 1H), 2.27 – 2.18 (m, 1H), 1.92 (ddddd, \( J = 13.5, 8.6, 7.3, 6.2 \) Hz, 1H). \(^{13}\)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 136.0, 134.2, 129.3, 128.8, 128.0, 126.3, 80.4, 60.1, 57.6, 26.1, 24.9.

\textbf{Trans-diastereomer (minor):} \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.33 (dd, \( J = 7.5, 1.6 \) Hz, 1H), 7.29 – 7.20 (m, 2H), 7.18 – 7.14 (m, 1H), 4.33 (d, \( J_{eq-eq} = 3.1 \) Hz, 1H), 3.75 (dt, \( J = 10.5, 3.1 \) Hz, 1H), 3.54 (s, 3H), 2.91 – 2.84 (m, 2H), 2.34 (ddddd, \( J = 12.9, 10.5, 8.9, 6.5 \) Hz, 1H), 2.01 – 1.96 (m, 1H). \(^{13}\)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 135.6, 134.1, 129.0, 128.6, 128.4, 125.8, 79.4, 58.8, 57.4, 26.9, 22.7.

(1-azido-2-methoxypropan-2-yl)benzene (3i)

Prepared according to general procedure A reacting \( \alpha \)-methylstyrene (325 \( \mu \)L). The title compound was obtained as a colourless oil (71 mg, 79%). Data are in accordance with previous literature reports. \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.46 – 7.35 (m, 4H), 7.36 – 7.28 (m, 1H), 3.45 (d, \( J = 12.5 \) Hz, 1H), 3.21 (d, \( J = 12.5 \) Hz, 1H), 3.14 (s, 3H), 1.65 (s, 3H). \(^{13}\)C NMR (125 MHz, Chloroform-\( d \)) \( \delta \) 141.8, 128.5, 127.8, 126.4, 79.5, 61.7, 50.6, 20.1. IR (neat film): 2932, 2097, 1446, 1073, 700. MS (EI): 135 (M - CH\(_2\)N\(_3\), 100). HRMS (EI): Calculated for C\(_9\)H\(_{11}\)O (M – CH\(_2\)N\(_3\)): 135.0804; Found: 135.0806.
2-azido-1,1-diphenyl-1-methoxyethane (3j)

Prepared according to general procedure A reacting \( \alpha \)-phenylstyrene (441 \( \mu \)L). The title compound was obtained as a colourless oil (102 mg, 80\%). \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.40 – 7.23 (m, 10H), 4.06 (s, 2H), 3.16 (s, 3H). \(^{13}\)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 142.2, 128.2, 127.6, 127.2, 82.8, 55.7, 51.2. IR (neat film): 2938, 2093, 1447, 1076, 715. MS (EI): 197 (M – CH\(_3\)N\(_3\)). HRMS (APCI): Calculated for C\(_{15}\)H\(_{15}\)O (M – N\(_3\)): 211.1123; Found: 211.1109.

(2-azido-1-methoxycyclohexyl)benzene (3k)

Prepared according to general procedure A reacting 1-phenylcyclohexene (398 \( \mu \)L). The title compound was obtained as a colourless oil (70 mg, 60\%).

**Cis-diestereomer (29 mg, 25\%):** \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.49 – 7.28 (m, 5H), 3.74 – 3.68 (m, 1H), 2.95 (s, 3H), 2.28 – 2.06 (m, 2H), 2.07 – 1.97 (m, 1H), 1.86 – 1.72 (m, 1H), 1.72 – 1.34 (m, 4H). \(^{13}\)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 142.4, 128.2, 127.8, 127.0, 78.7, 67.1, 49.4, 26.4, 24.4, 20.4, 19.6. IR (neat film, significant peaks): 2934, 2095, 1445, 1251, 1073, 698. MS (ESI): 254 (M + Na\(^+\)). HRMS (APCI): Calculated for C\(_{13}\)H\(_{14}\)NO (M + H\(^+\) - N\(_2\)): 204.1388; Found: 204.1381.

**Trans-diestereomer (41 mg, 35\%):** \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.45 – 7.27 (m, 5H), 3.17 (s, 3H), 3.06 (dd, \( J = 11.7, 4.0 \) Hz, 1H), 2.21 – 2.01 (m, 3H), 2.00 – 1.80 (m, 3H), 1.70 – 1.36 (m, 2H). \(^{13}\)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 141.7, 128.8, 127.4, 126.8, 80.4, 68.2, 49.9, 30.8, 27.1, 24.7, 20.6. IR (neat film, significant peaks): 2934, 2094, 1445, 1251, 1074, 699. MS (ESI): 254 (M + Na\(^+\)). HRMS (ESI): Calculated for C\(_{13}\)H\(_{15}\)N\(_3\)O (M + Na\(^+\)): 254.1269; Found: 254.1270.

(2-azido-1-methoxypropyl)benzene (3l)

Prepared according to general procedure A reacting \( \beta \)-methylstyrene (324 \( \mu \)L). The title compound was obtained as a colourless oil (32 mg, \( \text{syn:anti} = 2.2:1 \), 34\%). IR(neat): 2924, 2100, 1453, 1259, 1094, 702. MS (ESI): 214 (M + Na\(^+\)). HRMS (APCI): Calculated for C\(_{10}\)H\(_{14}\)NO (M + H\(^+\) - N\(_2\)): 164.1075; Found: 164.1084.

**Syn-diestereomer (major):** \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.44 – 7.27 (m, 5H), 4.18 (d, \( J = 4.9 \) Hz, 1H), 3.60 – 3.53 (m, 1H), 3.30 (s, 3H), 1.22 (d, \( J = 6.7 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 138.0, 128.4, 128.4, 127.4, 86.3, 61.4, 57.2, 14.3. IR (neat film): 2924, 2104, 1453, 1259, 1095, 702.

**Anti-diestereomer (minor):** \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.44 – 7.28 (m, 5H), 4.03 (d, \( J = 7.5 \) Hz, 1H), 3.67 – 3.61 (m, 1H), 3.26 (s, 3H), 0.98 (d, \( J = 6.7 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 138.3, 128.6, 128.2, 127.5, 87.9, 61.9, 57.0, 16.4.
2-azido-1,2-diphenyl-1-methoxyethane (3m)

Prepared according to general procedure A reacting cis-stilbene (446 µL). The title compound was obtained as a colourless oil (101 mg, syn:anti = 1:1.5, 80%), contaminated with small amounts of the diazide 4a. IR (neat film): 2928, 2909, 1453, 1254, 1101, 697. MS (EI): 225 (M - N2, 29), 210 (M - HN3, 85), 121 (M - C7H6N3, 100). HRMS (APCI): Calculated for C15H15O (M – N3): 211.1123; Found: 211.1121.

Anti-diastereomer (major): 1H NMR (400 MHz, Chloroform-d) δ 7.33 – 7.28 (m, 3H), 7.23 – 7.14 (m, 5H), 7.07 – 6.95 (m, 2H), 4.59 (d, J = 8.1 Hz, 1H), 4.31 (d, J = 8.1 Hz, 1H), 3.31 (s, 3H). 13C NMR (100 MHz, Chloroform-d) δ 137.6, 136.3, 128.2, 128.0, 127.8, 127.6, 87.8, 70.9, 57.1.

Syn-diastereomer (minor): 1H NMR (400 MHz, Chloroform-d) δ 7.33 – 7.28 (m, 3H), 7.23 – 7.14 (m, 5H), 7.07 – 6.95 (m, 2H), 4.71 (d, J = 6.3 Hz, 1H), 4.36 (d, J = 6.3 Hz, 1H), 3.19 (s, 3H). 13C NMR (100 MHz, Chloroform-d) δ 137.3, 136.4, 128.3, 128.2, 128.0, 127.9, 86.4, 70.0, 57.2.

(2-azido-1-methoxypropyl)-4-methoxybenzene (3n)

Prepared according to general procedure A reacting anethole (375 µL). The title compound was obtained as a colourless oil (97 mg, syn:anti = 1:2.8, 88%). MS (APCI): 194 (M – N2 + H+). HRMS (APCI): Calculated for C11H16NO2 (M – N2 + H+): 194.1141; Found: 194.1154.

Syn-diastereomer (minor): 1H NMR (500 MHz, Chloroform-d) δ 7.23 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 4.10 (d, J = 5.1 Hz, 1H), 3.82 (s, 3H), 3.56 (dd, J = 6.7, 5.1 Hz, 1H), 3.26 (s, 3H), 1.21 (d, J = 6.7 Hz, 3H). 13C NMR (125 MHz, Chloroform-d) δ 159.5, 129.9, 128.6, 113.8, 86.0, 61.5, 57.0, 55.3, 14.6. IR (neat film): 2910, 2095, 1511, 1096, 801.

Anti-diastereomer (major): 1H NMR (500 MHz, Chloroform-d) δ 7.20 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 3.97 (d, J = 7.6 Hz, 1H), 3.82 (s, 3H), 3.61 (dd, J = 7.6, 6.7 Hz, 1H), 3.23 (s, 3H), 0.96 (d, J = 6.7 Hz, 3H). 13C NMR (125 MHz, Chloroform-d) δ 159.7, 130.3, 128.6, 113.9, 87.4, 62.0, 56.7, 55.3, 16.3. IR (neat film): 2934, 2085, 1511, 1086, 828.

1-(2-azido-1-methoxyethyl)-4-fluorobenzene (3o)

Prepared according to general procedure A reacting 4-fluorostyrene (300 µL). The title compound was obtained as a colourless oil (49 mg, 50%), contaminated with small amounts of the diazide 4a. 1H NMR (500 MHz, Chloroform-d) δ 7.31 – 7.27 (m, 2H), 7.05 (t, J = 8.5 Hz, 2H), 4.34 (dd, J = 8.3, 3.8 Hz, 1H), 3.45 (dd, J = 12.9, 8.3 Hz, 1H), 3.30 (s, 3H), 3.19 (dd, J = 12.9, 3.8 Hz, 1H). 13C NMR (125 MHz, Chloroform-d) δ 162.9 (d, J = 248.5 Hz), 134.3 (d, J = 3.2 Hz), 128.4 (d, J = 8.2 Hz), 115.7 (d, J = 21.5 Hz), 82.5, 56.9, 56.5. 19F NMR (470 MHz, Chloroform-d) δ -114. IR (neat film): 2926, 2099, 1507, 1460, 1226, 1062, 834. IR (neat film): 2929, 2095, 1509, 1222, 1108, 833. MS (EI): 167 (M-
1-(2-azido-1-methoxyethyl)-4-chlorobenzene (3p)
Prepared according to general procedure A reacting 4-chlorostyrene (300 µL). The title compound was obtained as a colourless oil (71 mg, 67%). ¹H NMR (400 MHz, Chloroform-d) δ 7.36 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 4.34 (dd, J = 8.3, 3.7 Hz, 1H), 3.45 (dd, J = 12.9, 8.3 Hz, 1H), 3.30 (s, 3H), 3.19 (dd, J = 12.9, 3.7 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-d) δ 137.1, 134.2, 129.0, 128.0, 82.5, 57.0, 56.4. IR (neat film): 2929, 2098, 1438, 1114, 1097, 822. MS (EI): 185 (¹³ClM⁺ - N₂, 3), 183 (³⁵ClM⁺ - N₂, 10), 166 (³⁷ClM⁺ - HN₃, 4), 164 (³⁵ClM⁺ - HN₃, 12), 157 (³⁷ClM⁺ - CH₂N₃, 34), 155 (³⁵ClM⁺ - CH₂N₃, 100). HRMS (APCI): Calculated for C₉H₁₁NOF (M + H⁺ - N₂): 168.0825; Found: 168.0839.

2-(2-azido-1-methoxyethyl)benzothiophene (3q)
Prepared according to general procedure A reacting 2-vinylbenzothiophene (400 mg). The title compound was obtained as a yellow oil (93 mg, 80%), contaminated with small amounts of the diazide 4a. ¹H NMR (400 MHz, Chloroform-d) δ 7.88 – 7.81 (m, 1H), 7.80 – 7.72 (m, 1H), 7.39 – 7.31 (m, 2H), 7.28 (s, 1H), 4.69 (dd, J = 8.1, 3.9 Hz, 1H), 3.67 (dd, J = 12.8, 8.1 Hz, 1H), 3.42 (d, J = 1.0 Hz, 3H), 3.38 (dd, J = 13.0, 3.9 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-d) δ 142.8, 139.7, 139.2, 124.7, 124.5, 123.6, 122.9, 122.6, 79.4, 57.3, 56.3. IR (neat film): 2928, 2095, 1435, 1257, 1101, 772. MS (ESI): 256 (M + Na⁺). HRMS (APCI): Calculated for C₁₀H₉OS (M – CH₂N₃): 177.0374; Found: 177.0368.

2-(2-azido-1-methoxyethyl)benzofuran (3r)
Prepared according to general procedure A reacting 2-vinylbenzofuran (360 mg). The title compound was obtained as a colourless oil (67 mg, 62%). ¹H NMR (400 MHz, Chloroform-d) δ 7.60 – 7.56 (m, 1H), 7.51 – 7.47 (m, 1H), 7.31 (td, J = 7.6, 1.5 Hz, 1H), 7.28 – 7.21 (m, 1H), 6.77 (s, 1H), 4.53 (dd, J = 8.0, 4.2 Hz, 1H), 3.76 (dd, J = 13.0, 8.0 Hz, 1H), 3.50 (dd, J = 13.0, 4.2 Hz, 1H), 3.44 (s, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 155.1, 153.7, 127.7, 124.7, 123.0, 121.2, 111.5, 105.8, 76.8, 57.4, 53.6. IR (neat film): 2931, 2098, 1453, 1250, 1104, 809, 742. MS (EI): 217 (M, 1), 189 (M – N₂, 50), 161 (M – CH₂N₃, 100). HRMS (EI): Calculated for C₁₁H₁₁N₃O₂ (M⁺): 217.0846; Found: 217.0838.
1-(2-azido-1-methoxyethyl)-2-(prop-2-yn-1-yloxy)benzene (3s)

Prepared according to general procedure A reacting 2-(prop-2-yn-1-yloxy)styrene (578 mg) in methanol (5 mL). The title compound was obtained as a colourless oil (50 mg, 42%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.43 (dd, $J = 7.5, 1.8$ Hz, 1H), 7.30 (ddd, $J = 8.3, 7.5, 1.8$ Hz, 1H), 7.06 (td, $J = 7.5, 1.0$ Hz, 1H), 7.00 (dd, $J = 8.3, 1.0$ Hz, 1H), 4.85 (dd, $J = 7.6, 3.6$ Hz, 1H), 4.74 (d, $J = 2.4$ Hz, 2H), 3.36 (s, 3H), 3.39 – 3.29 (m, 2H), 2.50 (t, $J = 2.4$ Hz, 1H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 154.8, 128.9, 126.9, 121.8, 111.9, 78.3, 77.2, 75.7, 57.3, 55.9, 55.3. IR (neat film): 3290, 2929, 2099, 1601, 1487, 1220, 1103, 1023, 755. MS (EI): 231 (M, 10), 203 (M – N$_2$, 15), 175 (M – CH$_2$N$_2$, 100).

10-methoxy-10,11-dihydro-4H-benzo[g][1,2,3]triazolo[5,1-c][1,4]oxazocine (7)

Compound 3t (20 mg, 0.09 mmol) was dissolved in toluene (5 mL) and was heated up to 100 °C, stirring under nitrogen, for 72 hours. The solvent was removed at reduced pressure and the crude was purified using preparative thin layer chromatography. The title compound was obtained as a yellow oil (15 mg, 75%). $^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.33 (s, 1H), 7.30 (ddd, $J = 8.0, 7.3, 1.8$ Hz, 1H), 7.22 (dd, $J = 13.9, 7.0, 0.5$ Hz, 1H), 5.22 (d, $J = 14.3$ Hz, 1H), 5.04 (dd, $J = 13.9, 8.3$ Hz, 1H), 4.70 (dd, $J = 8.3, 7.0$ Hz, 1H), 3.37 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 155.8, 132.9, 132.5, 132.2, 130.8, 129.9, 125.3, 122.9, 81.2, 66.1, 56.9, 51.7. MS (ESI): 232 (M + H$^+$). HRMS (APCI): Calculated for C$_{12}$H$_{14}$N$_3$O$_2$ (M + H$^+$): 232.1086; Found: 232.1075.
5 Characterisation data for azido-functionalised compounds 4a, 5 and 6

![Chemical structure](image)

(1,2-diazidoethyl)benzene (4a)

Prepared according to general procedure C reacting styrene (90 µL) with sodium azide (325 mg) in acetonitrile (5 mL). The title compound was obtained as a colourless oil (90 mg, 96%). Data are in accordance with previous literature reports. $^1$H NMR (500 MHz, Chloroform-$d$) δ 7.45 – 7.36 (m, 3H), 7.36 – 7.31 (m, 2H), 4.67 (dd, $J = 8.3, 4.9$ Hz, 1H), 3.51 (dd, $J = 12.7, 8.3$ Hz, 1H), 3.45 (dd, $J = 12.7, 4.9$ Hz, 1H). $^{13}$C NMR (125 MHz, Chloroform-$d$) δ 136.3, 129.1, 129.1, 126.9, 65.5, 56.0. IR (neat film): 2936, 2089, 1454, 1253, 758, 698.

![Chemical structure](image)

2-azido-1-bromo-1-phenylethane (5)

Prepared according to general procedure C reacting styrene (290 µL) with sodium bromide (515 mg) in acetonitrile (5 mL). The title compound was obtained as a colourless oil (52 mg, 46%). Data are in accordance with previous literature reports. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.48 – 7.32 (m, 5H), 5.01 (t, $J = 7.3$ Hz, 1H), 3.93 – 3.83 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 138.5, 129.3, 129.1, 127.7, 57.6, 51.2. IR (neat film): 3031, 2925, 2100, 1454, 1259, 695. MS (EI): 199 (81 BrM – N$_2$, 20), 171 (81 BrM – CH$_2$N$_3$, 98), 169 (79 BrM – CH$_2$N$_3$, 100). HRMS (APCI): Calculated for C$_8$H$_9$N$_7$Br (M + H$^+$ - N$_2$): 197.9918; Found: 197.9926.

![Chemical structure](image)

(2-azido-1-(2,2,2-trifluoroethoxy)ethyl)benzene (6)

Prepared according to general procedure B reacting styrene (290 µL) in trifluoroethanol (5 mL). The title compound was obtained as a colourless oil (60 mg, 49%). $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.43 – 7.37 (m, 3H), 7.37 – 7.30 (m, 2H), 4.64 (dd, $J = 8.4, 3.6$ Hz, 1H), 3.80 (dq, $J = 12.0, 8.8$ Hz, 1H), 3.72 (dq, $J = 12.0, 8.4$ Hz, 1H), 3.59 (dd, $J = 13.2, 3.6$ Hz, 1H), 2.32 (dd, $J = 13.2, 3.6$ Hz, 1H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 136.8, 129.2, 129.1, 126.7, 123.8 (q, $J = 279$ Hz), 83.1, 66.1 (q, $J = 34$ Hz), 56.4. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ -74 (t, $J = 8.6$ Hz). IR (neat film): 2936, 2100, 1454, 1276, 1156, 1123, 960, 700. MS (EI): 217 (M – N$_2$, 2), 189 (M – CH$_2$N$_2$, 100). HRMS (EI): Calculated for C$_{10}$H$_{10}$NOF$_3$ (M – N$_2$): 217.0709; Found: 217.0709.
6. Characterisation data for diazido-functionalised compounds 4a – j and diamine 8

(1,2-diazidoethyl)benzene (4a)

Prepared according to general procedure D reacting styrene (290 μL) in methanol (5 mL). The title compound was obtained as a colourless oil (45 mg, 95%). Data are in accordance with previous literature reports.\(^1\) \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.45 – 7.36 (m, 3H), 7.36 – 7.31 (m, 2H), 4.67 (dd, \(J = 8.3, 4.9\) Hz, 1H), 3.51 (dd, \(J = 12.7, 8.3\) Hz, 1H), 3.45 (dd, \(J = 12.7, 4.9\) Hz, 1H). \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 136.3, 129.1, 129.1, 126.9, 65.5, 56.0. IR (neat film): 2936, 2089, 1454, 1253, 758, 698.

(1,2-diazidoethyl)-1,1-dibenzene (4b)

Prepared according to general procedure D reacting 1,1-diphenylethene (441 μL) in methanol (5 mL). The title compound was obtained as a colourless oil (47 mg, 72%). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.45 – 7.27 (m, 10H), 4.03 (s, 2H). \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 140.1, 128.7, 128.4, 127.4, 72.5, 59.4. IR (neat film): 2929, 2091, 1446, 1248, 756, 660. MS (APCI): 209 (M + H\(^+\) - N\(_4\)). HRMS (APCI): Calculated for C\(_{14}\)H\(_{13}\)N\(_2\) (M + H\(^+\) - N\(_4\)): 209.1079; Found: 209.1087.

1,2-diazido-1,2-diphenylethane (4c)

Prepared according to general procedure D reacting cis-stilbene (446 μL) in methanol (5 mL). The title compound was obtained as a colourless oil (25 mg, 38% of a 1:1.2 syn:anti mixture). Data are in accordance with previous literature reports.\(^1\)\(^2\) IR (neat film): 2093, 1453, 1243, 762, 698. Syn Product: \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.39 (dd, \(J = 5.2, 1.9\) Hz, 4H), 7.31 – 7.20 (m, 4H), 7.10 – 7.03 (m, 2H), 4.64 (s, 2H). \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 135.7, 128.7, 128.6, 127.7, 70.7. Anti Product: \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.39 (dd, \(J = 5.2, 1.9\) Hz, 4H), 7.31 – 7.20 (m, 4H), 7.10 – 7.03 (m, 2H), 4.69 (s, 2H). \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 135.8, 129.0, 128.7, 128.0, 69.6.
1-(1,2-diazidoethyl)-4-bromobenzene (4d)

Prepared according to general procedure D reacting 4-bromostyrene (327 μL) in methanol (5 mL). The title compound was obtained as a colourless oil (65 mg, 97%). Data are in accordance with previous literature reports.\(^{13}\) \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.55 (d, \(J = 8.4\) Hz, 2H), 7.22 (d, \(J = 8.4\) Hz, 1H), 3.48 (dd, \(J = 12.8, 8.0\) Hz, 1H), 3.42 (dd, \(J = 12.8, 5.0\) Hz, 1H). \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 135.4, 132.9, 128.6, 123.1, 64.9, 55.8. IR (neat film): 2917, 2092, 1489, 1250, 1010, 819. MS (EI): 211 \(^{81}\)BrM – N\(_4\), 19, 209 \(^{79}\)BrM – N\(_4\), 20, 184 \(^{81}\)BrM – N\(_2\) - CH\(_2\)N\(_3\), 98, 183 \(^{79}\)BrM – N\(_2\) - CH\(_2\)N\(_3\), 100, 157 \(^{81}\)BrM – C\(_2\)H\(_3\)N\(_6\), 49, 155 \(^{79}\)BrM – C\(_2\)H\(_3\)N\(_6\), 50.

1-(1,2-diazidoethyl)-4-chlorobenzene (4e)

Prepared according to general procedure D reacting 4-chlorostyrene (300 μL) in methanol (5 mL). The title compound was obtained as a colourless oil (38 mg, 68%). Data are in accordance with previous literature reports.\(^{13}\) \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.39 (d, \(J = 8.5\) Hz, 2H), 7.28 (d, \(J = 8.5\) Hz, 1H), 4.66 (dd, \(J = 8.0, 5.0\) Hz, 1H), 3.48 (dd, \(J = 12.8, 8.0\) Hz, 1H), 3.42 (dd, \(J = 12.8, 5.0\) Hz, 1H). \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 134.9, 129.4, 128.3, 64.8, 55.9. IR (neat film): 2926, 2090, 1492, 1331, 1250, 1091, 824. MS (EI): 139 \(^{37}\)ClM – N\(_2\) – CH\(_2\)N\(_3\), 35, 137 \(^{35}\)ClM – N\(_2\) – CH\(_2\)N\(_3\), 100.

1-(1,2-diazidoethyl)-4-cyanobenzene (4f)

Prepared according to general procedure D reacting 4-cyanostyrene (323 μL) in methanol (5 mL). The title compound was obtained as a colourless oil (26 mg, 49%). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.72 (d, \(J = 8.2\) Hz, 1H), 7.47 (d, \(J = 8.2\) Hz, 2H), 4.74 (dd, \(J = 7.3, 5.4\) Hz, 1H), 3.45 – 3.55 (m, 2H). \(^{13}\)C NMR (125 MHz, Chloroform-\(d\)) \(\delta\) 141.6, 132.9, 127.8, 118.2, 113.0, 64.8, 55.8. IR (neat film): 2927, 2229, 2093, 1253, 834.

1-(1,2-diazidoethyl)-4-trifluorobenzene (4g)
Prepared according to general procedure D reacting 4-trifluoromethylstyrene (369 μL) in methanol (5 mL). The title compound was obtained as a colourless oil (34 mg, 53%). $^1$H NMR (400 MHz, Chloroform-d$_2$) $\delta$ 7.61 (d, $J = 8.1$ Hz, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 4.67 (dd, $J = 7.9$, 5.0 Hz, 1H), 3.49 – 3.33 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-d$_2$) $\delta$ 140.4, 131.2 (q, $J = 32.7$ Hz), 130.72, 126.1 (q, $J = 3.8$ Hz), 123.8 (q, $J = 272.5$ Hz), 64.9, 55.9. $^{19}$F NMR (376 MHz, Chloroform-d$_2$) $\delta$ -62. IR (neat film): 2095, 1323, 1164, 1113, 1067, 839. MS (EI): 200 (M – N$_4$), 172 (M – CH$_2$N$_4$), 145 (M – C$_2$H$_3$N$_6$), 75. HRMS (APCI): Calculated for C$_9$H$_8$N$_2$F$_3$ (M + H$^+$ - N$_4$): 201.0640; Found: 201.0634.

1-(1,2-diazidopropan-2-yl)-4-fluorobenzene (4h)

Prepared according to general procedure D reacting 4-fluoro-$\alpha$-methylstylene (337 μL) in methanol (5 mL). The title compound was obtained as a colourless oil (44 mg, 80%). $^1$H NMR (400 MHz, Chloroform-d$_2$) $\delta$ 7.42 (dd, $J = 8.9$, 5.2 Hz, 2H), 7.09 (dd, $J = 8.9$, 8.3 Hz, 2H), 3.46 (d, $J = 12.5$ Hz, 1H), 3.39 (d, $J = 12.5$ Hz, 1H), 1.76 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-d$_2$) $\delta$ 162.4 (d, $J = 247.8$ Hz), 136.4 (d, $J = 3.4$ Hz), 127.7 (d, $J = 8.2$ Hz), 115.8 (d, $J = 21.5$ Hz), 66.1, 61.0, 22.4. $^{19}$F NMR (376 MHz, Chloroform-d$_2$) $\delta$ -113.7. IR (neat film): 2935, 2097, 1509, 1232, 1164, 833. MS (EI): 136 (M – CH$_2$N$_3$ – N$_2$).

2-(1,2-diazidoethyl)-naphthalene (4i)

Prepared according to general procedure D reacting 2-vinylnaphthalene (385 mg) in methanol (5 mL). The title compound was obtained as a colourless oil (57 mg, 92%). Data are in accordance with previous literature reports.

$^1$H NMR (400 MHz, Chloroform-d$_2$) $\delta$ 7.94 – 7.80 (m, 4H), 7.57 – 7.50 (m, 2H), 7.43 (dd, $J = 8.5$, 1.9 Hz, 1H), 4.85 (dd, $J = 8.4$, 4.9 Hz, 1H), 3.60 (dd, $J = 12.8$, 8.4 Hz, 1H), 3.52 (dd, $J = 12.8$, 4.9 Hz, 1H). $^{13}$C NMR (100 MHz, Chloroform-d$_2$) $\delta$ 133.6, 133.4, 133.1, 129.2, 128.1, 127.8, 126.8, 126.8, 126.6, 124.0, 65.8, 55.9. IR (neat film): 3056, 2927, 2092, 1252, 817, 746. MS (EI): 154 (M – CH$_2$N$_3$).

1,2-diazido-2,3-dihydro-1H-indene (4j)

Prepared according to general procedure D reacting indene (292 μL) in methanol (5 mL). The title compound was obtained as a colourless oil (38 mg, 76% of trans-isomer; 6 mg, 12% of cis-isomer). Data are in accordance with previous literature reports.

$^1$H NMR (400 MHz, Chloroform-d$_2$) $\delta$ 7.41 – 7.36 (m, 1H), 7.36 – 7.29 (m, 2H), 7.26 (q, $J = 3.1$, 2.6 Hz, 1H), 4.77 (d, $J = 5.6$ Hz, 1H), 4.23 – 4.10 (m, 1H), 3.35 (dd, $J = 16.0$, 7.3 Hz, 1H), 2.94 (dd, $J = 16.0$, 6.6 Hz, 1H). $^{13}$C NMR (100 MHz, Chloroform-d$_2$) $\delta$ 139.1, 137.7, 129.5, 127.8,
125.2, 124.6, 70.3, 67.7, 36.2. IR (neat film): 2920, 2091, 1317, 1253, 747. MS (El): 129 (M – HN₃ – N₂)

Cis-diastereomer: ¹H NMR (400 MHz, Chloroform-d) δ 7.40 – 7.25 (m, 4H), 4.84 (d, J = 5.6 Hz, 1H), 4.30 (q, J = 6.4 Hz, 1H), 3.22 – 3.10 (m, 2H). ¹³C NMR (100 MHz, Chloroform-d) δ 139.7, 137.5, 129.8, 127.7, 125.4, 125.0, 66.9, 64.1, 35.6. MS (El): 129 (M – HN₃ – N₂)

(1,2-diaminoethyl)benzene (8)

(1,2-diazidoethyl)benzene (90 mg, 0.48 mmol) was dissolved in ethanol (mL) and subjected to hydrogenation using the H-cube (Pd/C cartridge, 1 mL/min flow rate). Complete conversion was achieved and the title compound was obtained as a yellow solid (66 mg, 0.48 mmol, 100%). Data are in accordance with previous literature reports.¹⁵ ¹H NMR (400 MHz, Chloroform-d) δ 7.40 – 7.30 (m, 5H), 3.96 (dd, J = 7.4, 5.2 Hz, 1H), 2.96 (dd, J = 12.8, 5.2 Hz, 1H), 2.85 (dd, J = 12.8, 7.4 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-d) δ 143.7, 128.6, 127.4, 126.5, 57.7, 49.3. IR (neat film): 3287, 3029, 1637, 1549, 1478, 1317, 1288, 696. MS (ESI): 137 (M + H⁺).
7 $^1$H NMR, $^{13}$C NMR and IR spectra for methoxyazidated compounds 3a – t and oxazocine 7

Data for (2-azido-1-methoxyethyl)benzene (3a)
Data for 1-(2-azido-1-methoxyethyl)-2-methylbenzene (3b)
Data for 1-(2-azido-1-methoxyethyl)-3-methylbenzene (3c)
Data of 1-(2-azido-1-methoxyethyl)-4-methylbenzene (3d)
Data for 1-(2-azido-1-methoxyethyl)-2,4,6-trimethylbenzene (3e)
Data for 2-(2-azido-1-methoxyethyl)naphthalene (3f)
Data for 2-azido-1-methoxy-2,3-dihydro-1H-indene (3g)
Data for 2-azido-1-methoxy-1,2,3,4-tetrahydronaphthalene (3h)
Data for (1-azido-2-methoxypropan-2-yl)benzene (3i)
Data for 2-azido-1,1-diphenyl-1-methoxyethane (3j)
Data for (2-azido-1-methoxycyclohexyl)benzene (3k)

Cis-isomer
Trans-isomer
Data for (2-azido-1-methoxypropyl)benzene (3l)
Data for 2-azido-1,2-diphenyl-1-methoxyethane (3m)
Data for (2-azido-1-methoxypropyl)-4-methoxybenzene (3n)
Data for Methyl 1-(2-azido-1-methoxyethyl)-4-fluorobenzene (3o)
Data for 1-(2-azido-1-methoxyethyl)-4-chlorobenzene (3p)
Data for 2-(2-azido-1-methoxyethyl)benzothiophene (3q)
Data for 2-(2-azido-1-methoxyethyl)benzofuran (3r)
Data for 1-(2-azido-1-methoxyethyl)-2-(prop-2-yn-1-yloxy)benzene (3s)
Data for 1-(1-azido-2-methoxypropan-2-yl)-4-fluorobenzene (not in table)
Data for 10-methoxy-10,11-dihydro-4H-benzo[g][1,2,3]triazolo[5,1-c][1,4]oxazocine (7)
$^1$H NMR, $^{13}$C NMR and IR spectra for azido-functionalised compounds 4a, 5 and 6

Data for (1,2-diazidoethyl)benzene (4a)
Data for 2-azido-1-bromo-1-phenylethane (5)
for (2-azido-1-(2,2,2-trifluoroethoxy)ethyl)benzene (6)
9 $^1$H NMR, $^{13}$C NMR and IR spectra for diazido-functionalised compounds 4a-j

Data for (1,2-diazidoethyl)-1,1-dibenzene (4b)
Data for 1,2-diazido-1,2-diphenylethane (4c)
Data for 1-(1,2-diazidoethyl)-4-cyanobenzene (4f)
Data for 1-(1,2-diazidoethyl)-4-trifluorobenzene (4g)
Data for 1-(1,2-diazidopropan-2-yl)-4-fluorobenzene (4h)
Data for 1,2-diazido-2,3-dihydro-1H-indene (4j)
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