Supporting Information

Trichloroisocyanuric Acid-Mediated Oxidative Dehydrogenation of Hydrazines: A Practical Chemical Oxidation to Access Azo Compounds

Yingpeng Su,* Xuan Liu, Jie Yu, Guiyan Cao, Rong Zhang, Yanan Zhao, Danfeng Huang, Ke-Hu Wang, Congde Huo and Yulai Hu

College of Chemistry and Chemical Engineering, Northwest Normal University, 967Anning East Road, Lanzhou730070, P. R. China

* E-mail: suyp51@nwnu.edu.cn
Contents

I - General information....................................................................................................................... S4

II - General Procedure for the Oxidative dehydrogenation............................................................ S4

III - Datas and NMR copies ............................................................................................................... S5

(E)-1,2-diphenyldiazene (3a). ........................................................................................................... S5
(E)-1,2-bis(4-fluorophenyl)diazene (3b). .......................................................................................... S7
(E)-1,2-bis(4-chlorophenyl)diazene (3c). ....................................................................................... S9
(E)-1,2-bis(4-bromophenyl)diazene (3d). ..................................................................................... S11
(E)-1,2-bis(4-iodophenyl)diazene (3e). ......................................................................................... S13
(E)-1,2-bis(4-(trifluoromethyl)phenyl)diazene (3f). ................................................................. S15
(E)-1,2-di-p-tolyldiazene (3g). ......................................................................................................... S17
(E)-1,2-bis(4-methoxyphenyl)diazene (3h). .................................................................................. S19
(E)-1,2-bis(3-chlorophenyl)diazene (3i). ....................................................................................... S21
(E)-1,2-bis(2-chlorophenyl)diazene (3j). ....................................................................................... S23
(E)-1-(4-fluorophenyl)-2-phenyldiazene (3k). ............................................................................. S25
(E)-1-(4-chlorophenyl)-2-phenyldiazene (3l). .............................................................................. S27
(E)-1-(4-bromophenyl)-2-phenyldiazene (3m). ........................................................................... S29
(E)-1-(4-iodophenyl)-2-phenyldiazene (3n). .................................................................................. S31
(E)-1-phenyl-2-(4-(trifluoromethyl)phenyl)diazene (3o). ......................................................... S33
(E)-1-(4-methoxyphenyl)-2-phenyldiazene (3p). ........................................................................ S35
(E)-N,N-dimethyl-4-(phenyldiazenyl)aniline (3q). ....................................................................... S37
(E)-1-(3-chlorophenyl)-2-phenyldiazene (3r). .............................................................................. S39
(E)-1-(2-chlorophenyl)-2-phenyldiazene (3s). ............................................................................... S41
(E)-1-(3,5-bis(trifluoromethyl)phenyl)-2-phenyldiazene (3t). .................................................. S43
(E)-1-(2,4-dichlorophenyl)-2-phenyldiazene (3u). ...................................................................... S45
ethyl (E)-2-(4-fluorophenyl)diazene-1-carboxylate (3v) ..................................................... S47
ethyl (E)-2-(4-bromophenyl)diazene-1-carboxylate (3w) .................................................. S49
ethyl(E)-2-(4-nitrophenyl)diazene-1-carboxylate (3x) .......................................................... S51
ethyl (E)-2-(3,4-dichlorophenyl)diazene-1-carboxylate (3y) .................................................. S53
ethyl (E)-2-(p-tolyl)diazene-1-carboxylate (3z) .................................................................. S55
ethyl (E)-2-(4-methoxyphenyl)diazene-1-carboxylate (3aa) .................................................. S57
benzyl (E)-2-(4-bromophenyl)diazene-1-carboxylate (3ab) .................................................. S59
benzyl (E)-2-(4-nitrophenyl)diazene-1-carboxylate (3ac) ...................................................... S61
benzyl (E)-2-(p-tolyl)diazene-1-carboxylate (3ad) ............................................................... S63
benzyl (E)-2-(4-methoxyphenyl)diazene-1-carboxylate (3ae) ................................................ S65
i-butyl (E)-2-(4-nitrophenyl)diazene-1-carboxylate (3af) ...................................................... S67
t-butyl (E)-2-(4-nitrophenyl)diazene-1-carboxylate (3ag) ..................................................... S69
(9H-fluoren-9-yl)methyl (E)-2-(4-nitrophenyl)diazene-1-carboxylate (3ah) ....................... S71
(E)-N,N-diethyl-2-(4-nitrophenyl)diazene-1-carboxamide (3ai) ............................................. S73
IV - References ...................................................................................................................... S75
I - General information

All solvents were dried according to standard methods prior to use. All reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. Silica gel column chromatography was carried out using silica gel 60 (300–400 mesh). Analytical TLC was performed using silica gel (silica gel 60 F254). TLC plates were analyzed by exposure to UV light. \(^1\)H and \(^{13}\)C NMR spectra were recorded at 400 MHz or 600 MHz and 100 MHz or 150 MHz, respectively. NMR experiments were carried out in CDCl\(_3\) and are reported relative to internal TMS (\(\delta = 0.00\) for \(^1\)H NMR), residual CHCl\(_3\) (\(\delta = 7.26\) for \(^1\)H NMR and \(\delta = 77.00\) for \(^{13}\)C NMR). Melting points are uncorrected. HRMS were recorded on Q-Exactive and Micro TOF-QII mass instrument (ESI). All starting materials were prepared according to literature procedures: 1\(a^{1}\), 1\(b\)–1\(h^{2}\), 1\(i\)–1\(j^{3}\), 1\(k\)–1\(u^{2}\), 1\(v\)–1\(a^{4}\).

II - General Procedure for the Oxidative dehydrogenation

To a 10-mL flame-dried round-bottom flask equipped with a stirrer bar were added hydrazine 1 (0.3 mmol) and THF (1.5 mL). Then TCCA 2 (2.0 equiv) was added in portions and the resulting mixture was stirred at r.t. until all the starting material had been completely consumed (TLC monitoring; for reaction times see Tables 2 and 3). The mixture was evaporated under reduced pressure and the residue was purified by column chromatography (heptane/EtOAc 20:1–3:1) to obtain the desired azo compound 3.
III - Datas and NMR copies

*(E)-1,2-diphenyldiazene (3a).*

![](image)

**Compound 3a:** 97% yield; Orange solid, m.p. 67-68 °C.

**$^1$H NMR** (CDCl$_3$, 400 MHz) $\delta$ (ppm) 7.94 – 7.91 (m, 4H), 7.55–7.45 (m, 6H).

**$^{13}$C NMR** (CDCl$_3$, 100 MHz) $\delta$ (ppm) 152.6, 131.0, 129.1, 122.8.

**HRMS** (ESI) calcd for C$_{12}$H$_{11}$N$_2$ [M+H]$^+$ 183.09167, found 183.09171.
NMR copies of compound 3a:

$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 100 MHz, CDCl$_3$
(E)-1,2-bis(4-fluorophenyl)diazene (3b).

Compound 3b: 91% yield; Orange solid, m.p. 100-101 °C.

$^1\text{H NMR}$ (CDCl$_3$, 400 MHz) $\delta$ (ppm) 7.93–7.89 (m, 4H), 7.21–7.15 (m, 4H).

$^{13}\text{C NMR}$ (CDCl$_3$, 100 MHz) $\delta$ (ppm) 164.3 (d, $J = 250$ Hz), 148.9 (d, $J = 2.0$ Hz), 124.8 (d, $J = 9.0$ Hz), 116.0 (d, $J = 23$ Hz).

HRMS (ESI) calcd for C$_{12}$H$_9$F$_2$N$_2$ [M+H]$^+$ 219.07283, found 219.07283.
NMR copies of compound 3b:

$^1$H NMR 400 MHz, CDCl$_3$

$^1$C NMR 100 MHz, CDCl$_3$
(E)-1,2-bis(4-chlorophenyl)diazene (3c).

**Compound 3c:** 89% yield; Orange solid, m.p. 190-191 °C.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) 7.88–7.84 (m, 4H), 7.50–7.47 (m, 4H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) 150.8, 137.2, 129.4, 124.2.

HRMS (ESI) calcd for C$_{12}$H$_8$Cl$_2$N$_2$ [M+H]$^+$ 251.01373, found 251.01373.
NMR copies of compound 3c:

$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 100 MHz, CDCl$_3$
(E)-1,2-bis(4-bromophenyl)diazene (3d).

**Compound 3d**: 89% yield; Orange solid, m.p. 203-204 °C.

\[ \text{\textbf{\textsuperscript{1}H NMR (CDCl}_3, \textsuperscript{300 MHz) \delta (ppm) 7.79 (d, }J = 8.4 \text{ Hz, }4H\text{), 7.65 (d, }J = 8.4 \text{ Hz, }4H\text{).} } \]

\[ \text{\textbf{\textsuperscript{13}C NMR (CDCl}_3, \textsuperscript{100 MHz) \delta (ppm) 151.3, 132.4, 125.8, 124.4.} } \]

\[ \text{HRMS(ESI) calcd for C}_{12}\text{H}_9\text{Br}_2\text{N}_2 [M+H]^+ 338.91270, \text{found 338.91272.} \]
NMR copies of compound 3d:

\[ \text{\textsuperscript{1}H NMR 400 MHz, CDCl\textsubscript{3}} \]

\[ \text{\textsuperscript{13}C NMR 100 MHz, CDCl\textsubscript{3}} \]
(E)-1,2-bis(4-iodophenyl)diazene (3e).

![Image of compound 3e]

**Compound 3e:** 91% yield; Orange solid, m.p. > 230 °C.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) 7.88–7.85 (m, 4H), 7.66–7.62 (m, 4H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) 151.7, 138.4, 124.5, 98.1.

HRMS (ESI) calcd for C$_{12}$H$_9$I$_2$N$_2$ [M+H]$^+$ 434.88496, found 434.88495.
NMR copies of compound 3e:

\[ \text{\textsuperscript{1}H NMR 400 MHz, CDCl}_3 \]

\[ \text{\textsuperscript{13}C NMR 100 MHz, CDCl}_3 \]
(E)-1,2-bis(4-(trifluoromethyl)phenyl)diazene (3f).

![Chemical structure of compound 3f](image)

**Compound 3f**: 92% yield; Orange solid, m.p. 101-102 °C.

**1H NMR** (CDCl₃, 400 MHz) δ (ppm) 8.03 (d, J = 8.4 Hz, 4H), 7.80 (d, J = 8.0 Hz, 4H).

**13C NMR** (CDCl₃, 100 MHz) δ (ppm) 154.0, 133.0 (q, J = 32 Hz), 126.4 (q, J = 4 Hz), 123.8 (q, J = 270 Hz), 123.3.

NMR copies of compound 3f:
(E)-1,2-di-p-tolylidiazene (3g).

**Compound 3g**: 92% yield; Orange solid, m.p. 140-142 °C.

**1H NMR** (CDCl$_3$, 400 MHz) $\delta$ (ppm) 7.81 (d, $J = 8.4$ Hz, 4H), 7.30 (d, $J = 8.0$ Hz, 4H), 2.42 (s, 6H).

**13C NMR** (CDCl$_3$, 150 MHz) $\delta$ (ppm) 150.8, 141.2, 129.7, 122.7, 21.5.

**HRMS (ESI)** calcd for C$_{14}$H$_{15}$N$_2$ [M+H]$^+$ 211.12298, found 211.12305.
NMR copies of compound 3g:
(E)-1,2-bis(4-methoxyphenyl)diazene (3h).

Compound 3h: 82% yield; Orange solid, m.p. 163-165 °C.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) 7.88 (d, $J = 8.8$ Hz, 4H), 7.00 (d, $J = 9.2$ Hz, 4H), 3.88 (s, 6H).

$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ (ppm) 161.5, 147.1, 124.3, 114.1, 55.5.

HRMS (ESI) calcd for C$_{14}$H$_{15}$N$_2$O$_2$ [M+H]$^+$ 243.11280, found 243.11281.
NMR copies of compound 3h:

$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 150 MHz, CDCl$_3$
(E)-1,2-bis(3-chlorophenyl)diazene (3i).

\[
\begin{array}{c}
\text{Cl} \\
\text{N} \\
\text{N} \\
\text{Cl}
\end{array}
\]

**Compound 3i**: 87\% yield; Orange solid, m.p. 97-99 °C.

\[\text{^1H NMR (CDCl}_3, 400 MHz) \delta \text{ (ppm)} 7.91-7.89 (m, 2H), 7.85-7.83 (m, 2H), 7.48-7.47 (m, 4H).\]

\[\text{^13C NMR (CDCl}_3, 150 MHz) \delta \text{ (ppm)} 153.1, 135.2, 131.2, 130.2, 122.6, 121.9.\]

**HRMS (ESI)** calcd for C\textsubscript{12}H\textsubscript{9}Cl\textsubscript{2}N\textsubscript{2} [M+H]\textsuperscript{+} 251.01373, found 251.01382.
NMR copies of compound 3i:

$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 150 MHz, CDCl$_3$
(E)-1,2-bis(2-chlorophenyl)diazene (3j).

\[ \text{Compound 3j: 81% yield; Orange solid, m.p. 130-132 } ^\circ \text{C.} \]

\(^1\text{H NMR (CDCl}_3, \text{ 400 MHz) } \delta \text{ (ppm)} 7.79-7.76 \text{ (m, 2H)}, \text{ 7.58-7.56 } \text{ (m, 2H)}, \text{ 7.44-7.34 } \text{ (m, 4H).} \]

\(^{13}\text{C NMR (CDCl}_3, \text{ 150 MHz) } \delta \text{ (ppm)} 148.8, 135.8, 132.2, 130.7, 127.4, 118.1. \]

\( \text{HRMS (ESI) calcd for C}_{12}\text{H}_9\text{Cl}_2\text{N}_2 \text{ [M+H]}^+ 251.01373, \text{ found 251.01384.} \)
NMR copies of compound 3j:

$^1$H NMR 400 MHz, CDCl$_3$

$^1$C NMR 150 MHz, CDCl$_3$
(E)-1-(4-fluorophenyl)-2-phenyldiazene (3k).

Compound 3k: 88% yield; Orange solid, m.p. 77-79 °C.

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ (ppm) 7.94–7.89 (m, 4H), 7.51–7.43 (m, 3H), 7.19–7.15 (m, 2H).

$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ (ppm) 164.3 (d, $J = 250.5$ Hz), 152.4, 149.1 (d, $J = 3.0$ Hz), 131.0, 129.1, 124.8 (d, $J = 9.0$ Hz), 122.8, 116.0 (d, $J = 22.5$ Hz).

HRMS(ESI) calcd for C$_{12}$H$_{10}$FN$_2$ [M+H]$^+$ 201.08225, found 201.08244.
NMR copies of compound 3k:

\[ \text{\^1H NMR 600 MHz, CDCl}_3 \]

\[ \text{\^1C NMR 150 MHz, CDCl}_3 \]
(E)-1-(4-chlorophenyl)-2-phenyldiazene (3l).

Compound 3l: 89% yield; Orange solid, m.p. 86-87 °C.

$^{1}$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) 7.92 – 7.84 (m, 4H), 7.54 – 7.46 (m, 5H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) 152.4, 150.9, 136.9, 131.2, 129.3, 129.1, 124.1, 122.9.

HRMS(ESI) calcd for C$_{12}$H$_{10}$ClN$_2$ [M+H]$^+$ 217.05270, found 217.05270.
NMR copies of compound 31:

$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 100MHz, CDCl$_3$
(E)-1-(4-bromophenyl)-2-phenyldiazene (3m).

![Image of compound 3m]

**Compound 3m**: 92% yield; Orange solid, m.p. 87-88 °C.

**$^{1}$H NMR (CDCl$_3$, 400 MHz)** $\delta$ (ppm) 7.93 – 7.90 (m, 2H), 7.82 – 7.79 (m, 2H), 7.67 – 7.63 (m, 2H), 7.55 – 7.47 (m, 3H).

**$^{13}$C NMR (CDCl$_3$, 100 MHz)** $\delta$ (ppm) 152.4, 151.3, 132.3, 131.3, 129.1, 125.3, 124.3, 122.9.

**HRMS (ESI)** calcd for C$_{12}$H$_{10}$BrN$_2$ [M+H]$^+$ 261.00219, found 261.00217.
NMR copies of compound 3m:

$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 100 MHz, CDCl$_3$
(E)-1-(4-iodophenyl)-2-phenyldiazene (3n).

[Chemical structure image]

Compound 3n: 93% yield; Orange solid, m.p. 105-106 °C.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) 7.92 – 7.83 (m, 4H), 7.68 – 7.62 (m, 2H), 7.54 – 7.46 (m, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) 152.7, 152.1, 138.6, 131.6, 129.4, 124.7, 123.2, 97.9.

HRMS (ESI) calcd for C$_{12}$H$_{10}$IN$_2$ [M+H]$^+$ 308.98832, found 308.98822.
NMR copies of compound 3n:

$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 100 MHz, CDCl$_3$
(E)-1-phenyl-2-(4-(trifluoromethyl)phenyl)diazene (3o).

![Chemical Structure](image)

**Compound 3o**: 93% yield; Orange solid, m.p. 95-96 °C.

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ (ppm) 7.98 (d, $J$ = 8.4 Hz, 2H), 7.95 – 7.93 (m, 2H), 7.76 (d, $J$ = 8.4 Hz, 2H), 7.54 – 7.50 (m, 3H).

$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ (ppm) 154.4, 152.4, 132.2 (q, $J$ = 33 Hz), 131.8, 129.2, 126.3 (q, $J$ = 4.5 Hz), 123.9 (q, $J$ = 271.5 Hz), 123.2, 123.0.

HRMS(ESI) calcd for C$_{13}$H$_{10}$F$_3$N$_2$ [M+H]$^+$ 251.07906, found 251.07856.
NMR copies of compound 3o:

\[ \text{\^{1}H NMR 600 MHz, CDCl}_3 \]

\[ \text{\^{13}C NMR 150 MHz, CDCl}_3 \]
(E)-1-(4-methoxyphenyl)-2-phenyldiazene (3p).

**Compound 3p**: 88% yield; Orange solid, m.p. 53-54 °C.

$^1$H NMR (CDCl$_3$, 400 MHz) δ (ppm) 7.94 – 7.87 (m, 4H), 7.52 – 7.42 (m, 3H), 7.02 (d, $J = 8.8$ Hz, 2H), 3.89 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 162.0, 152.7, 147.0, 130.3, 129.0, 124.7, 122.5, 114.2, 55.6.

HRMS (ESI) calcd for C$_{13}$H$_{13}$N$_2$O [M+H]$^+$ 213.10224, found 213.10223.
NMR copies of compound 3p:
(E)-N,N-dimethyl-4-(phenyldiazenyl)aniline (3q).

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\end{array}
\]

**Compound 3q**: 90% yield; Orange solid, m.p. 115-116 °C.

\(^1\text{H NMR} \text{ (CDCl}_3\text{, }400 \text{ MHz}) \delta\text{ (ppm)} 7.90 - 7.83 \text{ (m, 4H)}, 7.49 - 7.45 \text{ (m, 2H); 7.39 - 7.35 \text{ (m, 1H), 6.76 \text{ (d, } J = 9.2 \text{ Hz, 2H), 3.08 \text{ (s, 6H).}}}

\(^{13}\text{C NMR} \text{ (CDCl}_3\text{, }100 \text{ MHz}) \delta\text{ (ppm)} 153.2, 152.4, 143.6, 129.3, 128.9, 124.9, 122.2, 111.5, 40.3.

**HRMS(ESI)** caled for C\text{_{14}H}_{16}\text{N}_3 [M+H]^+ 226.13387, found 226.13398.
NMR copies of compound 3q:

$^1$H NMR 400 MHz, CDCl$_3$

$^13$C NMR 100 MHz, CDCl$_3$
(E)-1-(3-chlorophenyl)-2-phenyldiazene (3r).

![Chemical Structure](image)

**Compound 3r**: 91% yield; Orange solid, m.p. 64-65 °C.

**$^{1}H$ NMR** (CDCl$_3$, 600 MHz) $\delta$ (ppm) 7.92–7.89 (m, 3H), 7.83–7.81 (m, 1H), 7.52–7.46 (m, 3H), 7.43–7.41 (m, 2H).

**$^{13}C$ NMR** (CDCl$_3$, 150 MHz) $\delta$ (ppm) 153.4, 152.3, 135.1, 131.5, 130.6, 130.1, 129.1, 123.0, 122.3, 121.7.

**HRMS** (ESI) calcd for C$_{12}$H$_{10}$ClN$_{2}$ [M+H]$^+$ 217.05270, found 217.05273.
NMR copies of compound 3r:

\[ \text{\textsuperscript{1}H NMR 600 MHz, CDCl}_3 \]

\[ \text{\textsuperscript{13}C NMR 150 MHz, CDCl}_3 \]
(E)-1-(2-chlorophenyl)-2-phenyldiazene (3s).

\[
\begin{align*}
\text{Compound 3s: } & \text{ 82\% yield; Orange oil.} \\
\text{1H NMR (CDCl}_3, 400 MHz) \delta (ppm) & \text{ 7.99–7.97 (m, 2H), 7.71–7.69 (m, 1H), 7.57–7.50 (m, 4H),} \\
& \text{ 7.42–7.33 (m, 2H).} \\
\text{13C NMR (CDCl}_3, 150 MHz) \delta (ppm) & \text{ 152.8, 148.7, 135.3, 131.6, 131.5, 130.7, 129.1, 127.3, 123.3,} \\
& \text{ 117.6.} \\
\text{HRMS(ESI) calcd for C}_{12}\text{H}_{10}\text{ClN}_2 [M+H]^+ & \text{ 217.05270, found 217.05270.}
\end{align*}
\]
NMR copies of compound 3s:

$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 150 MHz, CDCl$_3$
(E)-1-(3,5-bis(trifluoromethyl)phenyl)-2-phenyldiazene (3t).

Compound 3t: 93% yield; Orange solid, m.p. 70-71 °C.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) 8.36 (s, 2H), 7.99–7.96 (m, 3H), 7.57–7.55 (m, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) 152.8, 152.0, 132.7 (q, $J = 34$ Hz), 132.5, 129.3, 123.8 (q, $J = 4$ Hz), 123.4, 123.1 (q, $J = 271$ Hz), 123.0 (q, $J = 4$ Hz).

HRMS (ESI) calcd for C$_{14}$H$_9$F$_6$N$_2$ [M+H]$^+$ 319.06644, found 319.06644.
NMR copies of compound 3t:
(E)-1-(2,4-dichlorophenyl)-2-phenyldiazene (3u).

Compound 3u: 93% yield; Orange solid, m.p. 107-108 °C.

\(^1\text{H NMR}\) (CDCl\textsubscript{3}, 400 MHz) \(\delta\) (ppm) 7.96–7.94 (m, 2H), 7.66 (d, \(J = 8.8\) Hz, 1H), 7.56 (d, \(J = 2.4\) Hz, 1H), 7.54–7.47 (m, 3H), 7.30 (dd, \(J = 8.8, 2.0\) Hz, 1H).

\(^{13}\text{C NMR}\) (CDCl\textsubscript{3}, 100 MHz) \(\delta\) (ppm) 152.6, 147.1, 137.1, 136.2, 131.8, 130.4, 129.2, 127.7, 123.4, 118.4.

HRMS(ESI) calcd for C\(_{12}\)H\(_9\)Cl\(_2\)N\(_2\) [M+H]\(^+\) 251.01373, found 251.01375.
NMR copies of compound 3u:
ethyl \((E)\)-2-(4-fluorophenyl)diazene-1-carboxylate (3v).

\[
\begin{align*}
\text{Compound 3v:} & \quad 92\% \text{ yield; Orange oil.} \\
^1H \text{ NMR (CDCl}_3, \text{ 400 MHz}) & \quad \delta \text{ (ppm) 8.00–7.96 (m, 2H), 7.27–7.19 (m, 2H), 4.52 (q, } J = 7.2 \text{ Hz, 2H), 1.47 (t, } J = 7.2 \text{ Hz, 3H).} \\
^{13}C \text{ NMR(CDCl}_3, \text{ 100 MHz}) & \quad \delta \text{ (ppm) 166.1 (d, } J = 255 \text{ Hz), 161.9, 148.1 (d, } J = 3 \text{ Hz), 126.2 (d, } J = 9.0 \text{ Hz), 116.5(d, } J = 23 \text{ Hz), 64.5, 14.1.} \\
\text{HRMS(ESI) calcd for C}_{9}H_{10}FN_{2}O_{2} [M+H]^+} & \quad 197.07208, \text{ found 197.07207.}
\end{align*}
\]
NMR copies of compound 3v:

$^1$H NMR 400 MHz, CDCl$_3$

$^1$C NMR 100 MHz, CDCl$_3$
ethyl (E)-2-(4-bromophenyl)diazene-1-carboxylate (3w).

![Chemical Structure](image)

**Compound 3w**: 91% yield; Orange oil.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) 7.82–7.79 (m, 2H), 7.69–7.67 (m, 2H), 4.53 (q, $J = 7.2$ Hz, 2H), 1.47 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) 161.9, 150.2, 132.7, 128.9, 125.1, 64.6, 14.1.

HRMS (ESI) calcd for C$_9$H$_{10}$BrN$_2$O$_2$ [M+H]$^+$ 256.99202, found 256.99158.
NMR copies of compound 3w:

**H NMR 400 MHz, CDCl₃**

**C NMR 100 MHz, CDCl₃**

S50
ethyl\((E)\)-2-(4-nitrophenyl)diazene-1-carboxylate (3x).

\[
\text{\chem{N\backslash N\backslash N\backslash O\backslash O}}
\]

**Compound 3x**: 94% yield; Orange solid, m.p. 58-59 °C.

\(^1\text{H NMR}\) (CDCl\(_3\), 400 MHz) \(\delta\) (ppm) 8.42–8.39 (m, 2H), 8.08–8.04 (m, 2H), 4.56 (q, \(J = 7.2\) Hz, 2H), 1.49 (t, \(J = 7.2\) Hz, 3H).

\(^{13}\text{C NMR}\) (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 161.5, 154.2, 150.3, 124.8, 124.2, 65.0, 14.1.

**HRMS**(ESI) calcd for C\(_9\)H\(_{10}\)N\(_3\)O\(_4\) [M+H]\(^+\) 224.06658, found 224.06596.
NMR copies of compound 3x:

1H NMR 400 MHz, CDCl₃

13C NMR 100 MHz, CDCl₃
ethyl (E)-2-(3,4-dichlorophenyl)diazene-1-carboxylate (3y).

![Chemical Structure](image)

**Compound 3y**: 92% yield; Orange solid, m.p. 43-44 °C.

\(^1\text{H NMR}\) (CDCl\(_3\), 400 MHz) \(\delta\) (ppm) 8.02 (d, \(J = 2.4\) Hz, 1H), 7.81 (dd, \(J = 8.4, 2.4\) Hz, 1H), 7.64 (d, \(J = 8.8\) Hz, 1H), 4.53 (q, \(J = 7.2\) Hz, 2H), 1.48 (t, \(J = 7.2\) Hz, 3H).

\(^{13}\text{C NMR}\) (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 161.6, 150.2, 138.1, 134.0, 131.2, 124.6, 123.6, 64.8, 14.1.

\textbf{HRMS}(ESI) calcd for C\(_9\)H\(_7\)Cl\(_2\)N\(_2\)O\(_2\) [M-H]\(^-\) 244.98791, found 244.99680.
NMR copies of compound 3y:

$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 100 MHz, CDCl$_3$
ethyl (E)-2-(p-tolyl)diazene-1-carboxylate (3z).

Compound 3z: 90% yield; Orange oil.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) 7.85 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 4.52 (q, $J = 7.2$ Hz, 2H), 2.45 (s, 3H) 1.47 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) 162.2, 149.8, 145.2, 130.0, 123.9, 64.3, 21.7, 14.2.

HRMS (ESI) calcd for C$_{10}$H$_{13}$N$_2$O$_2$ [M+H]$^+$ 193.09715, found 193.09712.
NMR copies of compound 3z:

$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 100 MHz, CDCl$_3$
ethyl (E)-2-(4-methoxyphenyl)diazene-1-carboxylate (3aa).

\[
\begin{align*}
\text{Compounds 3aa:} & \quad 86\% \text{ yield; Orange oil.} \\
^{1}H \text{ NMR (CDCl}_3, 400 \text{ MHz}) & \quad \delta (\text{ppm}) 7.99 - 7.95 (\text{m, 2H}), 7.03 - 6.99 (\text{m, 2H}), 4.51 (\text{q, } J = 7.2 \text{ Hz, 2H}), 3.91 (\text{s, 3H}) 1.47 (\text{t, } J = 7.2 \text{ Hz, 3H}). \\
^{13}C \text{ NMR (CDCl}_3, 100 \text{ MHz}) & \quad \delta (\text{ppm}) 164.6, 162.1, 146.1, 126.5, 114.5, 64.2, 55.7, 14.2. \\
\text{HRMS(ESI) calcd for C}_{10}H_{13}N_2O_3 \ [M+H]^+ & \quad 209.09207, \text{ found 209.09203.}
\end{align*}
\]
NMR copies of compound 3aa:
benzyl (E)-2-(4-bromophenyl)diazene-1-carboxylate (3ab).

![Structure of compound 3ab]

**Compound 3ab**: 93% yield; Orange solid, m.p. 75-76 °C.

**$^1$H NMR** (CDCl₃, 400 MHz) $\delta$ (ppm) 7.80 – 7.75 (m, 2H), 7.66 – 7.64 (m, 2H), 7.49 – 7.46 (m, 2H), 7.43 – 7.35 (m, 3H), 5.46 (s, 2H).

**$^{13}$C NMR** (CDCl₃, 100 MHz) $\delta$ (ppm) 161.8, 150.2, 134.2, 132.6, 128.9, 128.9, 128.7, 128.7, 125.1, 70.0.

**HRMS** (ESI) calcd for C₁₄H₁₂BrN₂O₂ [M+H]$^+$ 319.00767, found 319.00052.
NMR copies of compound **3ab**:

**$^1$H NMR 400 MHz, CDCl$_3$**

**$^{13}$C NMR 100 MHz, CDCl$_3$**
benzyl (E)-2-(4-nitrophenyl)diazene-1-carboxylate(3ac).

Compound 3ac: 95% yield; Orange solid, m.p. 116-118 °C.

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ (ppm) 8.39 – 8.37 (m, 2H), 8.05 – 8.02 (m, 2H), 7.49 – 7.48 (m, 2H), 7.43 – 7.38 (m, 3H), 5.49 (s, 2H).

$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ (ppm) 161.4, 154.2, 150.3, 134.0, 129.1, 128.8, 128.8, 124.8, 124.3, 70.4.

HRMS (ESI) calcd for C$_{14}$H$_{10}$N$_3$O$_4$ [M-H]$^-$ 284.06658, found 284.06772.
NMR copies of compound 3ac:

\[ \text{H NMR 600 MHz, CDCl}_3 \]

\[ \text{C NMR 150 MHz, CDCl}_3 \]
benzyl (E)-2-(p-tolyl)diazene-1-carboxylate (3ad).

**Compound 3ad**: 88% yield; Orange oil.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) 7.85-7.82 (m, 2H), 7.50-7.47 (m, 2H), 7.42-7.36 (m, 3H), 7.32-7.29 (m, 2H), 5.46 (s, 2H), 2.43 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) 162.1, 149.8, 145.3, 134.5, 129.9, 128.8, 128.7, 128.7, 124.0, 69.8, 21.7.

HRMS (ESI) calcd for C$_{15}$H$_{13}$N$_2$O$_2$ [M-H]$^-$ 253.09715, found 253.09718.
NMR copies of compound 3ad:

$^{1}H$ NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 100 MHz, CDCl$_3$
benzyl (E)-2-(4-methoxyphenyl)diazene-1-carboxylate (3ae).

**Compound 3ae:** 85% yield; Orange solid, m.p. 44-45 °C.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) 7.97–7.93 (m, 2H), 7.50–7.47 (m, 2H), 7.42–7.34 (m, 3H), 7.00–6.96 (m, 2H), 5.45 (s, 2H), 3.88 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ (ppm) 164.7, 162.0, 146.1, 134.6, 128.7, 128.7, 128.6, 126.5, 114.4, 69.6, 55.7.

HRMS (ESI) calcd for C$_{15}$H$_{15}$N$_2$O$_3$ [M+H]$^+$ 271.10772, found 271.10770.
NMR copies of compound 3ae:

\[ \text{\textsuperscript{1}H NMR 400 MHz, CDCl}_3 \]

\[ \text{\textsuperscript{13}C NMR 150 MHz, CDCl}_3 \]
i-butyl (E)-2-(4-nitrophenyl)diazene-1-carboxylate (3af).

**Compound 3af:** 95% yield; Orange solid, m.p. 41-43 °C.

\[ ^1H \text{NMR (CDCl}_3, 400 MHz) \delta (ppm) 8.43–8.39 (m, 2H), 8.08–8.05 (m, 2H), 4.28 (d, } J = 6.8 \text{ Hz, 2H), 2.21–2.11 (m, 1H), 1.05 (d, } J = 6.8 \text{ Hz, 6H).} \]

\[ ^{13}C \text{NMR (CDCl}_3, 100 MHz) \delta (ppm) 161.7, 154.2, 150.2, 124.8, 124.2, 74.6, 27.8, 18.8. \]

**HRMS (ESI) calcd for C_{11}H_{12}N_{3}O_{4} [M-H]^− 250.08223, found 250.08266.**
NMR copies of compound 3af:

**1H NMR 400 MHz, CDCl₃**

**13C NMR 100 MHz, CDCl₃**
$t$-butyl $(E)$-2-(4-nitrophenyl)diazene-1-carboxylate (3ag).

**Compound 3ag:** 95% yield; Orange solid, m.p. 135-136 °C.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) 8.41–8.37 (m, 2H), 8.04–8.01 (m, 2H), 1.68 (s, 9H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) 160.5, 154.4, 150.1, 124.7, 124.1, 86.1, 27.8.

HRMS (ESI) calcd for C$_{11}$H$_{12}$N$_3$O$_4$ [M-H]$^-$ 250.08223, found 250.08490.
NMR copies of compound 3ag:
(9H-fluoren-9-yl)methyl (E)-2-(4-nitrophenyl)diazene-1-carboxylate (3ah).

[Chemical structure image]

**Compound 3ah:** 88% yield; Orange solid, m.p. 126-128 °C.

**^1H NMR** (CDCl₃, 400 MHz) δ (ppm) 8.43–8.39 (m, 2H), 8.11–8.07 (m, 2H), 7.79 (d, J = 7.6 Hz, 2H), 7.68–7.61 (m, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 4.75–4.72 (m, 2H), 4.41 (t, J = 7.2 Hz, 1H).

**^13C NMR** (CDCl₃, 100 MHz) δ (ppm) 161.5, 154.2, 150.4, 142.8, 141.3, 128.1, 127.3, 125.1, 124.8, 124.4, 120.2, 70.4, 46.5.

NMR copies of compound 3ah:

$^1$H NMR 400 MHz, CDCl$_3$

$^1$C NMR 100 MHz, CDCl$_3$
(E)-N,N-diethyl-2-(4-nitrophenyl)diazene-1-carboxamide (3ai).

Compound 3ai: 91% yield; Orange solid, m.p. 101-103 °C.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) 8.40 (d, $J = 8.8$ Hz, 2H), 8.04 (d, $J = 8.8$ Hz, 2H), 3.61 (q, $J = 6.8$ Hz, 2H), 3.52 (q, $J = 7.2$ Hz, 2H), 1.34 (t, $J = 6.8$ Hz, 3H), 1.20 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) 161.2, 154.7, 149.8, 124.7, 123.9, 41.9, 41.7, 14.4, 12.8.

HRMS(ESI) calcd for C$_{11}$H$_{15}$N$_4$O$_3$ [M+H]$^+$ 251.11387, found 251.11383.
NMR copies of compound 3ai:

\[ \text{H NMR 400 MHz, CDCl}_3 \]

\[ \text{C NMR 100 MHz, CDCl}_3 \]
IV - References