Supporting Information

Palladium-Catalyzed Direct \textit{ortho}-Sulfonylation of Azobenzenes with Arylsulfonyl Chlorides \textit{via} C–H Activation

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1. General Information
All the chemicals were obtained commercially and used without any prior purification. \(^1\)HNMR spectra were recorded on a Bruker AvanceII 500 spectrometer. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90°C) and ethyl acetate, unless otherwise noted. All compounds were characterized by \(^1\)H NMR, \(^{13}\)C NMR and HRGC–HRMS, which are consistent with those reported in the literature.

2. Experimental Section
General procedure for preparation of azoxybenzenes

\[
\begin{align*}
\text{R}^1\text{H}_2\text{CuBr} (6 \text{ mol\%}) & \quad \text{pyridine} (18 \text{ mol\%}) \\
\text{N} & \quad \text{air} (1 \text{ atm}) \\
\text{toluene} (2 \text{ml}) & \quad \text{R}^2\text{N} = \text{N}\text{R}^1\text{R}^2
\end{align*}
\]

All of the azo-compounds were prepared from arylamines, according to the literature.\(^{[1]}\) Mix CuBr (4.2 mg, 0.03 mmol), pyridine (8.7 mg, 0.09 mmol), arylamines (93 mg, 1 mmol) in toluene (4 ml) under air (1 atm). The reaction mixture was vigorously stirred at 60 °C for 20 h. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether) to afford azo-compound; yellow solid;

General procedure for preparation ortho-sulfonylated azobenzenes

\[
\begin{align*}
\text{N} & \quad \text{Pd(CN)}_2\text{Cl}_2 (10 \text{ mol\%}) \\
\text{S} & \quad \text{K}_2\text{CO}_3 (2 \text{ equiv}) \\
\text{O} & \quad 4A \text{ MS} (100 \text{ mg}) \\
\text{O} & \quad 1,4\text{-dioxane} (2 \text{ ml}) \\
1a & \quad \text{Cl-S} \\
\text{2a} & \quad \text{N} = \text{N}
\end{align*}
\]

Mix azoic compound (0.5equiv), benzene sulfonyl chloride (0.6equiv), Pd(CH\(_3\)CN\(_2\))\(_2\)Cl\(_2\) (10 mol%), K\(_2\)CO\(_3\) (2 equiv), 4A MS (100 mg) in 1,4-dioxane (2 ml) under air. The reaction mixture was vigorously stirred at 130 °C for 12 h. After
cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel to afford the protect.

3. Characterization data of the products

Diazene. (1a)

(E)-1,2-di-p-tolylidazene.

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

Obtained as a yellow solid in 90% yield; M.p. 138-140 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.81 \text{ (d, } J = 8.3 \text{ Hz, } 4\text{H}), 7.30 \text{ (d, } J = 8.0 \text{ Hz, } 4\text{H}), 2.42 \text{ (s, } 6\text{H}). \)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 150.85, 141.22, 129.73, 122.75, 21.50. \)

HRMS (ESI+): Calculated for C\(_{14}\)H\(_{14}\)N\(_2\): [M+H]\(^+\) 211.123, Found 211.1032.

(E)-1,2-di-m-tolylidazene

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

Obtained as a yellow solid in 87% yield; M.p. 123-124 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.71 \text{ (s, } 4\text{H}), 7.40 – 7.34 \text{ (m, } 2\text{H}), 7.25 \text{ (d, } J = 7.0 \text{ Hz, } 2\text{H}), 2.42 \text{ (d, } J = 3.0 \text{ Hz, } 6\text{H}). \)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 152.87, 139.00, 131.75, 128.95, 122.97, 120.54, 21.43. \)

HRMS (ESI+): Calculated for C\(_{14}\)H\(_{14}\)N\(_2\): [M+H]\(^+\) 211.123, Found 211.1034.

(E)-1,2-bis(4-ethoxyphenyl)diazene.

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

Obtained as a yellow solid in 92% yield; M.p. 150-151 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.91 – 7.82 \text{ (m, } 4\text{H}), 7.40 – 7.34 \text{ (m, } 2\text{H}), 6.98 \text{ (d, } J = 8.9 \text{ Hz, } 4\text{H}), 4.10 \text{ (q, } J = 7.0 \text{ Hz, } 4\text{H}), 1.44 \text{ (t, } J = 7.0 \text{ Hz, } 6\text{H}). \)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 161.01, 146.93, 124.36, 114.66, 63.79, 14.80. \)

HRMS (ESI+): Calculated for C\(_{16}\)H\(_{18}\)N\(_2\)O\(_2\): [M+H]\(^+\) 211.123, Found 211.1032.

(E)-1,2-bis(3-methoxyphenyl)diazene.

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

Obtained as a yellow solid in 85% yield; M.p. 70-71 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.49 \text{ (ddd, } J = 7.8, 1.6, 0.9 \text{ Hz, } 2\text{H}), 7.40 – 7.37 \text{ (m, } 2\text{H}), 7.36 \text{ (t, } J = 8.0 \text{ Hz, } 2\text{H}), 6.98 \text{ (ddd, } J = 8.2, 2.6, 0.8 \text{ Hz, } 2\text{H}), 3.83 \text{ (s, } 6\text{H}). \)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 159.31, 152.79, 128.76, 116.85, 116.14, 104.69, 54.46. \)

HRMS (ESI+): Calculated for
C_{14}H_{14}N_{2}O_{2}: [M+H]^+ 243.1128, Found 243.0686.

(E)-1-(3-methoxyphenyl)-2-phenyldiazene.

Obtained as a yellow solid in 60% yield; M.p. 30-31 °C.

\[ \text{NMR (500 MHz, CDCl}_3\] δ 7.95 – 7.89 (m, 2H), 7.57 – 7.41 (m, 6H), 7.07 – 7.02 (m, 1H), 3.90 (s, 3H).

\[ \text{C NMR (126 MHz, CDCl}_3\] δ 160.34, 153.91, 152.61, 131.05, 129.80, 129.11, 122.89, 117.83, 117.14, 105.74, 55.50. HRMS (ESI+): Calculated for C_{13}H_{12}N_{2}O: [M+H]^+ 213.1022, Found 213.061.

(E)-1-(3-methoxyphenyl)-2-(m-tolyl)diazene.

Obtained as a yellow liquid in 58% yield.

\[ \text{NMR (500 MHz, CDCl}_3\] δ 7.73 (d, J = 5.8 Hz, 2H), 7.55 (ddd, J = 7.8, 1.5, 1.0 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.41 (dd, J = 16.4, 8.3 Hz, 2H), 7.29 (d, J = 7.5 Hz, 1H), 7.03 (ddd, J = 8.2, 2.6, 0.8 Hz, 1H), 3.89 (s, 3H), 2.45 (s, 3H), 2.45 (s, 1H).

\[ \text{C NMR (126 MHz, CDCl}_3\] δ 160.32, 153.94, 152.68, 138.99, 131.83, 129.76, 128.91, 122.93, 120.55, 117.72, 117.04, 105.69, 55.47, 21.37. HRMS (ESI+): Calculated for C_{14}H_{14}N_{2}O: [M+H]^+ 227.075.

(E)-1-phenyl-2-(2-tosylphenyl)diazene (3a)

Obtained as a white solid in 78% yield; M.p. 157-158 °C. \[ \text{NMR (500 MHz, CDCl}_3\] δ 8.40 (dd, J = 7.7, 1.5 Hz, 1H), 7.86 – 7.80 (m, 4H), 7.65 (dd, J = 22.0, 7.5, 1.4 Hz, 2H), 7.58 (dd, J = 7.7, 1.3 Hz, 1H), 7.55 – 7.50 (m, 3H), 7.16 (d, J = 8.2 Hz, 2H), 2.32 (s, 3H). \[ \text{C NMR (126 MHz, CDCl}_3\] δ 152.72, 149.07, 143.91, 139.43, 138.88, 134.35, 131.97, 130.54, 129.35, 129.29, 129.11, 128.20, 123.77, 116.90, 21.51. HRMS (ESI+): Calculated for C_{23}H_{18}N_{2}O_{3}S: [M+H]^+ 336.0916, Found 337.0989.

(E)-1-(2-((4-bromophenyl)sulfonyl)phenyl)-2-phenyldiazene (3b)
Obtained as a orange solid in 66% yield; M.p. 200-201 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.39 (d, J = 7.8 Hz, 1H), 7.84 – 7.78 (m, 4H), 7.71 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.52 – 7.48 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 152.68, 148.96, 141.34, 138.17, 134.82, 132.20, 131.96, 129.78, 129.42, 129.23, 128.20, 123.67, 117.06. HRMS (ESI+): Calculated for C₁₈H₁₃BrN₂O₂S: [M+Na]+ 422.9773, Found 422.9178.

(E)-1-(2-((4-fluorophenyl)sulfonyl)phenyl)-2-phenyldiazene(3c)

Obtained as a orange solid in 86% yield; M.p. 107-108 °C.
¹H NMR (500 MHz, CDCl₃) δ 8.40 (dd, J = 7.8, 1.4 Hz, 1H), 8.00 – 7.95 (m, 2H), 7.83 – 7.79 (m, 2H), 7.70 (dd, J = 7.7, 1.5 Hz, 1H), 7.65 (td, J = 7.6, 1.4 Hz, 1H), 7.60 (dd, J = 7.8, 1.3 Hz, 1H), 7.57 – 7.53 (m, 3H), 7.03 (t, J = 8.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 152.69, 148.95, 138.43, 134.70, 132.16, 131.12, 131.05, 130.67, 129.35, 129.21, 123.66, 117.04, 116.01, 115.83. HRMS (ESI+): Calculated for C₁₈H₁₃FN₂O₂S: [M+Na]+ 341.0755, Found 341.0211.

(E)-1-(2-((4-nitrophenyl)sulfonyl)phenyl)-2-phenyldiazene (3d)

Obtained as a pale yellow solid in 67% yield; M.p. 134-135 °C.
¹H NMR (500 MHz, CDCl₃) δ 8.44 (d, J = 7.8 Hz, 1H), 8.19 (d, J = 8.2 Hz, 2H), 8.13 (d, J = 8.5 Hz, 2H), 7.74 (qd, J = 15.1, 7.5 Hz, 4H), 7.65 (d, J = 7.9 Hz, 1H), 7.55 (d, J = 5.8 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 152.57, 150.15, 148.90, 148.06, 137.29, 135.42, 132.50, 130.92, 129.65, 129.36, 123.90, 123.57, 117.21. HRMS (ESI+): Calculated for C₁₈H₁₃N₃O₄S: [M+H]+ 368.07, Found 368.0128.

(E)-1-(2-((4-methoxyphenyl)sulfonyl)phenyl)-2-phenyldiazene (3e)
Obtained as a white solid in 75% yield; M.p. 139-140 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.37 (d, $J = 7.7$ Hz, 1H), 7.87 (dd, $J = 20.9$, 6.6 Hz, 4H), 7.64 (dt, $J = 21.9$, 7.4 Hz, 2H), 7.55 (dd, $J = 12.8$, 6.5 Hz, 4H), 6.82 (d, $J = 8.4$ Hz, 2H), 3.76 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.21, 152.75, 149.02, 139.16, 134.23, 133.81, 131.95, 130.54, 129.16, 123.75, 116.92, 113.87, 55.57. HRMS (ESI+): Calculated for C$_{19}$H$_{16}$N$_2$O$_3$S: [M+H]$^+$ 353.0954, Found 4353.0419.

(E)-1-(2-((3-nitrophenyl)sulfonyl)phenyl)-2-phenyldiazene (3f)

Obtained as a yellow solid in 63% yield; M.p. 162-163 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.92 (s, 1H), 8.46 (d, $J = 7.8$ Hz, 1H), 8.32 (d, $J = 8.1$ Hz, 1H), 8.23 (d, $J = 7.8$ Hz, 1H), 7.79 (dd, $J = 3.1$, 2.1 Hz, 2H), 7.77 – 7.68 (m, 2H), 7.64 (d, $J = 7.8$ Hz, 1H), 7.56 (ddd, $J = 9.7$, 5.2, 4.3 Hz, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 152.48, 148.85, 147.95, 144.55, 137.37, 135.39, 133.71, 132.55, 130.89, 130.09, 129.61, 129.39, 127.50, 123.75, 123.59, 117.29. HRMS (ESI+): Calculated for C$_{18}$H$_{13}$N$_3$O$_4$S: [M+H]$^+$ 368.07, Found 368.0146.

(E)-1-(2-(naphthalen-2-ylsulfonyl)phenyl)-2-phenyldiazene (3g)

Obtained as a pale yellow solid in 84% yield; M.p. 139-140 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.64 (s, 1H), 8.64 (s, 1H), 8.57 – 8.44 (m, 1H), 8.57 – 8.46 (m, 1H), 8.46 (dd, $J = 22.7$, 8.8 Hz, 3H), 7.78 (d, $J = 8.1$ Hz, 3H), 7.70 (ddd, $J = 9.2$, 6.0, 1.8 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.57 – 7.47 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 152.72, 149.00, 138.98, 138.59, 134.97, 134.59, 132.01, 131.95, 130.63, 130.19, 129.46, 129.17, 129.11, 128.96, 127.87, 127.36, 123.76, 123.03, 116.89. HRMS (ESI+): Calculated for C$_{22}$H$_{16}$N$_2$O$_3$S: [M+H]$^+$ 373.1005, Found 373.0445.
(E)-3,5-dimethyl-4-((2-(phenyldiazenyl)phenyl)sulfonyl)isoxazole. (3h)

Obtained as a white solid in 90% yield; M.p. 101–102 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.37 (d, J = 7.9 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.73 – 7.65 (m, 3H), 7.56 (dd, J = 12.3, 7.0 Hz, 4H), 2.50 (s, 3H), 2.19 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 174.00, 157.64, 152.98, 149.64, 137.80, 135.01, 132.19, 130.43, 129.24, 129.13, 123.30, 117.89, 117.64, 13.04, 10.81. HRMS (ESI+): Calculated for C₁₇H₁₅N₃O₃S: [M+H]+ 342.0907, Found 342.0377.

(E)-1-phenyl-2-(2-(thiophen-2-ylsulfonyl)phenyl)diazene. (3i)

Obtained as a white solid in 87% yield; M.p. 100–101 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.37 (d, J = 8.0 Hz, 1H), 8.06 – 7.98 (m, 2H), 7.82 – 7.77 (m, 1H), 7.76 – 7.69 (m, 2H), 7.68 – 7.63 (m, 1H), 7.63 – 7.53 (m, 4H), 7.00 (t, J = 4.4 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 152.67, 149.00, 143.44, 139.35, 134.53, 134.38, 134.06, 132.12, 130.82, 129.25, 129.21, 127.23, 124.09, 116.89. HRMS (ESI+): Calculated for C₁₆H₁₂N₂O₂S₂: [M+H]+ 329.0413, Found 329.0336.

(E)-1-(2-((5-chloro-3-methylbenzo[b]thiophen-2-yl)sulfonyl)phenyl)-2-phenyldiazene. (3j)

Obtained as a pale yellow solid in 89% yield; M.p. 156–157 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.45 (d, J = 7.7 Hz, 1H), 7.87 (d, J = 7.5 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.73 – 7.63 (m, 1H), 7.52 (q, J = 5.3 Hz, 1H), 7.38 (d, J = 8.7 Hz, 1H), 2.51 (d, J = 0.6 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 152.46, 149.41, 140.55, 139.83, 138.46, 137.09, 134.91, 132.15, 131.31, 130.53, 129.58, 128.98, 127.89, 124.12, 123.63, 123.21, 117.17, 12.35. HRMS (ESI+): Calculated for C₂₁H₁₅N₂O₂S₂: [M+H]+ 427.0336, Found 426.9721.
(E)-methyl 3-((2-(phenyldiazenyl)phenyl)sulfonyl)thiophene-2-carboxylate. (3k)

Obtained as a pale yellow solid in 73% yield; M.p. 92-93 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(^{\text{δ}}\) 8.54 (dd, \(J = 5.6, 3.6 \text{ Hz}, 1\)H), 7.85 (d, \(J = 5.2 \text{ Hz}, 1\)H), 7.79 – 7.71 (m, 1H), 7.68 – 7.61 (m, 1H), 7.49 (d, \(J = 7.6 \text{ Hz}, 1\)H), 7.39 (d, \(J = 5.3 \text{ Hz}, 1\)H), 3.71 (s, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(^{\text{δ}}\) 159.44, 154.45, 152.40, 151.33, 146.00, 145.89, 139.06, 134.18, 132.02, 131.79, 130.11, 130.09, 128.90, 123.69, 116.34, 52.59. HRMS (ESI+): Calculated for C\(_{18}\)H\(_{14}\)N\(_2\)O\(_4\)S\(_2\): [M+H]+ 387.0468, Found 386.9885.

(E)-1-phenyl-2-(2-(phenylsulfonyl)phenyl)diazene. (3l)

Obtained as a orange solid in 90% yield; M.p. 149-150 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(^{\text{δ}}\) 8.43 (dd, \(J = 7.8, 1.5 \text{ Hz}, 1\)H), 7.95 (dt, \(J = 6.3, 2.0 \text{ Hz}, 2\)H), 7.83 – 7.75 (m, 2H), 7.68 (dd, \(J = 22.5, 7.5, 1.5 \text{ Hz}, 2\)H), 7.62 – 7.58 (m, 1H), 7.54 – 7.50 (m, 3H), 7.49 – 7.45 (m, 1H), 7.37 (dd, \(J = 10.6, 4.9 \text{ Hz}, 2\)H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(^{\text{δ}}\) 146.56, 143.29, 142.32, 138.53, 134.56, 132.96, 132.04, 130.59, 129.46, 129.11, 128.66, 128.05, 123.77, 116.92. HRMS (ESI+): Calculated for C\(_{18}\)H\(_{14}\)N\(_2\)O\(_4\)S\(_2\): [M+H]+ 356.0395, Found 357.0432.

(E)-1-(2-((4-chlorophenyl)sulfonyl)phenyl)-2-phenyldiazene. (3m)

Obtained as a orange solid in 82% yield; M.p. 170-171 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(^{\text{δ}}\) 8.40 (dd, \(J = 7.8, 1.4 \text{ Hz}, 1\)H), 7.93 – 7.86 (m, 2H), 7.84 – 7.76 (m, 2H), 7.71 (td, \(J = 7.6, 1.5 \text{ Hz}, 1\)H), 7.65 (td, \(J = 7.6, 1.4 \text{ Hz}, 1\)H), 7.63 – 7.58 (m, 1H), 7.57 – 7.51 (m, 3H), 7.37 – 7.30 (m, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(^{\text{δ}}\) 152.65, 148.94, 140.76, 139.61, 138.19, 134.79, 132.17, 130.68, 129.69, 129.40, 129.20, 128.95, 123.65, 117.03. HRMS (ESI+): Calculated for C\(_{18}\)H\(_{14}\)N\(_2\)O\(_4\)S\(_2\): [M+H]+ 322.0776, Found 323.0832.
(E)-1-(2-((4-(tert-butyl)phenyl)sulfonyl)phenyl)-2-phenyldiazene. (3n)

Obtained as an orange solid in 91% yield; M.p. 140-141 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.41 (dd, $J$ = 7.7, 1.5 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.81 – 7.74 (m, 2H), 7.70 – 7.60 (m, 2H), 7.57 – 7.54 (m, 1H), 7.53 – 7.49 (m, 3H), 7.38 – 7.32 (m, 2H), 1.22 (d, $J$ = 3.3 Hz, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 156.81, 152.66, 149.13, 139.31, 138.77, 134.40, 131.98, 130.54, 129.28, 129.07, 127.89, 125.71, 123.78, 116.92, 35.08, 31.00. HRMS (ESI+): Calculated for C$_{18}$H$_{14}$N$_2$O$_4$S$_2$: [M+H]$^+$ 378.1402, Found 379.1446.

(E)-1-(4-methyl-2-tosylphenyl)-2-(p-tolyl)diazene(3o)

Obtained as an orange solid in 86% yield; M.p. 174-175 °C.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.23 (s, 1H), 7.87 (d, $J$ = 8.3 Hz, 2H), 7.74 (d, $J$ = 8.2 Hz, 2H), 7.55 (d, $J$ = 8.1 Hz, 1H), 7.47 (dd, $J$ = 8.1, 1.1 Hz, 1H), 7.33 (d, $J$ = 8.1 Hz, 2H), 7.19 (d, $J$ = 8.1 Hz, 2H), 2.54 (s, 3H), 2.48 (s, 3H), 2.34 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 150.91, 147.03, 143.72, 142.46, 141.26, 139.60, 138.53, 134.88, 129.73, 129.62, 129.23, 128.14, 123.73, 116.73, 21.61, 21.53, 21.45. HRMS (ESI+): Calculated for C$_{21}$H$_{20}$N$_2$O$_2$S: [M+H]$^+$ 365.1318, Found 365.076.

(E)-1-(5-methyl-2-tosylphenyl)-2-(m-tolyl)diazene. (3p)

Obtained as a white solid in 75% yield; m. p. 96-97 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.30 (d, $J$ = 8.1 Hz, 1H), 7.86 (d, $J$ = 8.3 Hz, 2H), 7.67 (d, $J$ = 7.9 Hz, 1H), 7.60 (s, 1H), 7.48 – 7.40 (m, 2H), 7.40 – 7.32 (m, 2H), 7.20 (d, $J$ = 8.1 Hz, 2H), 2.48 (d, $J$ = 10.1 Hz, 6H), 2.35 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$
(E)-1-(4-ethoxy-2-tosylphenyl)-2-(4-ethoxyphenyl)diazene. (3q)

Obtained as a white solid in 83% yield; M.p. 95-96 °C. 1H NMR (500 MHz, CDCl₃) δ 7.91 (d, J = 2.7 Hz, 1H), 7.86 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 8.9 Hz, 2H), 7.69 (d, J = 8.9 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.16 – 7.13 (m, 1H), 7.02 – 6.99 (m, 2H), 4.23 (q, J = 7.0 Hz, 2H), 4.16 (d, J = 7.0 Hz, 2H), 2.34 (s, 3H), 1.52 (d, J = 6.9 Hz, 3H), 1.49 (d, J = 6.9 Hz, 3H).

13C NMR (126 MHz, CDCl₃) δ 161.77, 160.33, 147.13, 143.71, 142.76, 140.11, 139.61, 129.22, 128.07, 125.53, 120.75, 118.35, 114.60, 113.75, 64.55, 63.90, 21.53, 14.77, 14.65.


(E)-1-(5-methoxy-2-tosylphenyl)-2-(3-methoxyphenyl)diazene. (3r)

Obtained as an orange solid in 85% yield; M. p. 139–140 °C. 1H NMR (500 MHz, CDCl₃) δ 8.33 (d, J = 8.7 Hz, 1H), 7.85 (d, J = 8.3 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.14 – 7.08 (m, 3H), 3.93 (s, 3H), 3.90 (s, 3H), 2.33 (s, 3H).13C NMR (126 MHz, CDCl₃) δ 164.15, 160.33, 153.79, 150.71, 143.56, 140.06, 131.45, 130.97, 129.82, 129.31, 127.80, 118.86, 118.10, 116.19, 106.73, 101.29, 55.98, 55.56, 21.51.


(E)-1-(3-methoxyphenyl)-2-(2-tosylphenyl)diazene. (3s)

Obtained as an orange solid in 15% yield; M.p. 73-74 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.39 \text{ (dd, } J = 7.7, 1.5 \text{ Hz, 1H}), 7.85 \text{ (d, } J = 8.3 \text{ Hz, 2H}), 7.70 - 7.61 \text{ (m, 2H}), 7.58 \text{ (dd, } J = 7.7, 1.4 \text{ Hz, 1H}), 7.50 - 7.42 \text{ (m, 2H)}, 7.37 \text{ (dd, } J = 5.0, 3.1 \text{ Hz, 1H}), 7.17 \text{ (d, } J = 8.0 \text{ Hz, 2H}), 7.12 - 7.07 \text{ (m, 1H)}. \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 160.42, 149.01, 143.93, 139.37, 138.70, 137.02, 134.38, 130.58, 129.80, 129.46, 129.35, 128.12, 128.76, 117.98, 116.93, 106.76, 55.56, 21.55. HRMS (ESI+): Calculated for C\(_{20}\)H\(_{18}\)N\(_2\)O\(_3\)S: [M+H]+ 367.1111, Found 367.0548.

\[^{(-)}\]1-(5-methoxy-2-tosylphenyl)-2-phenyldiazene.(3t)

Obtained as an orange solid in 71% yield; M.p. 70-71 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.32 \text{ (d, } J = 8.7 \text{ Hz, 1H}), 7.84 - 7.79 \text{ (m, 4H}), 7.55 - 7.50 \text{ (m, 3H)}, 7.15 \text{ (d, } J = 8.1 \text{ Hz, 2H}), 7.12 - 7.07 \text{ (m, 2H)}, 3.89 \text{ (s, 3H)}, 2.31 \text{ (s, 3H)}. \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 164.13, 152.57, 150.71, 143.54, 140.00, 132.05, 131.36, 131.11, 129.23, 129.12, 127.94, 123.84, 116.15, 101.22, 55.97, 21.51. HRMS (ESI+): Calculated for C\(_{20}\)H\(_{18}\)N\(_2\)O\(_3\)S: [M+H]+ 367.1111, Found 367.0548.

\[^{(-)}\]1-(5-methoxy-2-tosylphenyl)-2-(m-tolyl)diazene.(3u)

Obtained as an orange solid in 81% yield; M.p. 70-71 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.32 \text{ (d, } J = 8.8 \text{ Hz, 1H}), 7.83 \text{ (d, } J = 8.3 \text{ Hz, 2H}), 7.65 \text{ (d, } J = 7.8 \text{ Hz, 1H}), 7.58 \text{ (s, 1H)}, 7.41 \text{ (t, } J = 7.7 \text{ Hz, 1H}), 7.34 \text{ (d, } J = 7.5 \text{ Hz, 1H}), 7.17 \text{ (d, } J = 8.3 \text{ Hz, 2H}), 7.10 \text{ (dd, } J = 8.8, 2.6 \text{ Hz, 1H}), 7.07 \text{ (d, } J = 2.6 \text{ Hz, 1H)}, 3.89 \text{ (s, 3H)}, 2.47 \text{ (s, 3H)}, 2.33 \text{ (s, 3H)}. \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 164.14, 152.67, 150.79, 143.48, 140.06, 138.98, 132.84, 131.35, 130.95, 129.22, 128.92, 127.89, 123.93, 121.57, 116.04, 101.19, 55.95, 21.53, 21.37. HRMS (ESI+): Calculated for C\(_{21}\)H\(_{20}\)N\(_2\)O\(_3\)S: [M+H]+ 381.1267, Found 381.0685.
4. $^1$H and $^{13}$C NMR spectra of the products

$^1$H NMR

$^{13}$C NMR
**$^{1}$H NMR**

**$^{13}$C NMR**
$^{1}H$ NMR

$^{13}C$ NMR
$^1$H NMR

$^{13}$C NMR
$^{1}H$ NMR

$^{13}C$ NMR
$^{1}H$ NMR

$^{13}C$ NMR
**H NMR**

[Chemical structures and NMR spectra are shown, with peaks at specific ppm values.]
$^{13}$C NMR

$^{1}$H NMR
$\text{H NMR}$

$\text{13C NMR}$
$^{1}H$ NMR
$^{13}$C NMR

$^1$H NMR
$\text{H NMR}$

$\text{C NMR}$

$\text{13C NMR}$
5. X-ray Crystal Data for GPT-Pd catalyst 3b

Crystals of GPT-Pd catalyst 3c (C_{18}H_{13}BrN_{2}O_{2}S) were recrystallized from a trichloromethane solution. A single white needle crystal which was suitable for X-ray diffraction measurements was mounted on a glass fiber. Unit cell measurements and intensity data collections were performed on a Rigaku AFC7R diffractometer with graphite monochromated Mo Ka. The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXTL-97 program suite. Direct methods yielded all non-hydrogen atoms which were refined with anisotropic thermal parameters. The reflection data were consistent with a monoclinic system: P2(1)/c. The obtained crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 1057250 (CCDC NO). The crystallographic data and refinement parameters of 3c are listed in Table S1.
Table S1. Crystallographic data and structure refinement for 3b.

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6. References