Organocatalytic Oxidation of Substituted Anilines to Azoxybenzenes and Nitrocompounds: Mechanistic Studies Excluding the Involvement of a Dioxirane Intermediate

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General Remarks

Chromatographic purification of products was accomplished using forced-flow chromatography on Merck® Kieselgel 60 F_{254} 230-400 mesh. Thin-layer chromatography (TLC) was performed on aluminum backed silica plates (0.2 mm, 60 F_{254}). Visualization of the developed chromatogram was performed by fluorescence quenching using phosphomolybdic acid, anisaldehyde or potassium permanganate stains. Melting points were determined on a Buchi® 530 hot stage apparatus and are uncorrected. Mass spectra (ESI) were recorded on a Finningan® Surveyor MSQ LC-MS spectrometer. HRMS spectra were recorded on Bruker® Maxis Impact QTOF spectrometer. ^1H, ^19F and ^13C NMR spectra were recorded on Varian® Mercury (200 MHz, 188 MHz and 50 MHz respectively), and are internally referenced to residual solvent signals. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad signal, bs m = broad signal multiplet), coupling constant and assignment. Data for ^13C NMR are reported in terms of chemical shift (δ ppm). Mass spectra and conversions of the reactions were recorded on a Shimadzu® GCMS-QP2010 Plus Gas Chromatograph Mass Spectrometer utilizing a MEGA® column (MEGA-5, F.T : 0.25μm, I.D. : 0.25mm, L : 30m, T_{max} : 350 °C, Column ID# 11475). Acetonitrile (HPLC grade, CHEM-LAB) was employed for the reactions. Normal grade MeCN led to lower yields for the nitro compounds (increased amount of azoxybenzenes). Water (HPLC grade, Merck) was used to prepare the aqueous buffer.
Reaction Optimization for the Organocatalytic Oxidation of Aniline to Diphenyldiazene Oxide 2a

![Chemical Structure](image)

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General Procedure for the Organocatalytic Synthesis of Diazene Oxides

Substituted aniline (1.00 mmol) was placed in a round bottom flask and dissolved in ethanol (0.5 mL), followed by 2,2,2-trifluoro-1-phenylethanone (17.4 mg, 0.10 mmol). Aqueous buffer solution (0.5 mL, 0.6 M K$_2$CO$_3$ – 4 x 10$^{-4}$M EDTA disodium salt), acetonitrile (0.075 mL, 1.50 mmol) and 30% aqueous H$_2$O$_2$ (0.18 mL, 1.50 mmol) were added consecutively. The reaction mixture was left stirring for 18 hours at room temperature. The crude product was purified using flash column chromatography (5% EtOAc in Pet. Ether) to afford the desired product.

1,2-Diphenyldiazene oxide (2a)

Yellow liquid; 94% yield; $^1$H NMR (CDCl$_3$) $\delta$: 8.32 (2H, d, $J = 8.3$ Hz ArH), 8.12 (2H, d, $J = 8.3$ Hz ArH), 7.58-7.36 (6H, m, ArH); $^{13}$C NMR (CDCl$_3$) $\delta$: 148.3, 143.9, 131.5, 129.6, 128.7, 128.6, 125.5, 122.3; MS (ESI) 199 (M+H$^+$, 100%).

1,2-Bis(4-chlorophenyl)diazeny oxide (2b)

Yellow solid; mp 144-147 °C; 88% yield; $^1$H NMR (CDCl$_3$) $\delta$: 8.34-8.08 (4H, m, ArH), 7.53-7.37 (4H, m, ArH); $^{13}$C NMR (CDCl$_3$) $\delta$: 146.5, 142.1, 138.0, 135.2, 129.5, 129.0, 128.9, 127.0, 124.9, 123.6; MS (ESI) 267 (M+H$^+$, 100%).
1,2-Bis(4-bromophenyl)diazene oxide (2c)¹

Orange solid; mp 164-166 °C; 89% yield; ¹H NMR (CDCl₃) δ: 8.18 (2H, d, J = 8.8 Hz, ArH), 8.08 (2H, d, J = 8.8 Hz, ArH), 7.65 (2H, d, J = 8.8 Hz, ArH), 7.61 (2H, d, J = 8.8 Hz, ArH); ¹³C NMR (CDCl₃) δ: 142.5, 132.5, 132.0, 127.2, 126.4, 123.8, 123.6; MS (ESI) 357 (M+H⁺, 100%).

1,2-Bis(4-fluorophenyl)diazene oxide (2d)²

Yellow solid; mp 84-86 °C; 89% yield; ¹H NMR (CDCl₃) δ: 8.38-8.19 (4H, m, ArH), 7.31-7.09 (4H, m, ArH); ¹³C NMR (CDCl₃) δ: 164.5 (d, J = 252.8 Hz), 162.5 (d, J = 252.8 Hz), 144.5, 140.2, 127.9 (d, J = 8.5 Hz), 124.5 (d, J = 9.3 Hz), 115.9 (d, J = 3.4 Hz), 115.5 (d, J = 2.5 Hz); ¹⁹F NMR (CDCl₃) δ: -53.0, -53.6; MS (ESI) 235 (M+H⁺, 100%).

1,2-Di-p-tolyldiazene oxide (2e)¹

Orange solid; mp 150-151 °C; 91% yield; ¹H NMR (CDCl₃) δ: 8.18 (2H, d, J = 8.8 Hz, ArH), 8.14 (2H, d, J = 8.8 Hz, ArH), 7.28 (4H, d, J = 8.8 Hz, ArH), 2.42 (3H, s, CH₃), 2.40 (3H, s, CH₃); ¹³C NMR (CDCl₃) δ: 146.1, 141.8, 141.7, 139.9, 129.2, 129.1, 125.6, 122.0, 21.5, 21.2; MS (ESI) 227 (M+H⁺, 100%).
1,2-Bis(4-hexylphenyl)diazene oxide (2f)

Brown solid; mp 75-78 °C; 84% yield; $^1$H NMR (CDCl$_3$) $\delta$: 8.22 (2H, d, $J =$ 8.7 Hz, ArH), 8.18 (2H, d, $J =$ 8.7 Hz, ArH), 7.29 (4H, d, $J =$ 8.7 Hz, ArH), 2.67 (4H, t, $J =$ 7.4 Hz, 2 x CH$_2$), 1.76-1.48 (4H, m, 2 x CH$_2$), 1.43-1.15 (12H, m, 6 x CH$_2$), 0.91 (6H, t, $J =$ 6.2 Hz, 2 x CH$_3$); $^{13}$C NMR (CDCl$_3$) $\delta$: 146.7, 146.2, 144.9, 141.9, 128.9, 128.5, 125.6, 122.0, 35.8, 35.5, 31.6, 31.1, 28.9, 28.8, 22.5, 14.0; HRMS exact mass calculated for [M+Na]$^+$ (C$_{24}$H$_{34}$N$_2$NaO$_7$) requires m/z 389.2563, found m/z 389.2568.

1,2-Di(biphenyl-4-yl)diazene oxide (2g)$^3$

Yellow solid; mp 197-199 °C; 88% yield; $^1$H NMR (CDCl$_3$) $\delta$: 8.32-8.24 (4H, m, ArH), 7.76-7.57 (8H, m, ArH), 7.55-7.38 (6H, m, ArH); $^{13}$C NMR (CDCl$_3$) $\delta$: 147.8, 144.1, 143.3, 142.3, 140.1, 139.5, 129.0, 128.8, 128.2, 127.8, 127.4, 127.2, 127.1, 126.2, 122.8; MS (ESI) 351 (M+H$^+$, 100%).

1,2-Bis(4-ethoxyphenyl)diazene oxide (2h)$^4$

Orange solid; mp 137-139 °C; 95% yield; $^1$H NMR (CDCl$_3$) $\delta$: 8.30-8.13 (4H, m, ArH), 6.98-6.86 (4H, m, Ar), 4.14-4.01 (4H, m, 2 x OCH$_2$), 1.48-1.38 (6H, m, 2 x CH$_3$); $^{13}$C NMR (CDCl$_3$)
δ: 161.1, 159.5, 141.4, 137.7, 127.7, 123.6, 114.1, 113.9, 63.9, 63.6, 14.6, 14.5; MS (ESI) 287 (M+H+, 100%).

1,2-Bis(4-methoxyphenyl)diazenec oxide (2i)

Yellow solid; mp 111-113 °C; 92% yield; $^1$H NMR (CDCl$_3$) δ: 8.37-8.13 (4H, m, ArH), 7.06-6.87 (4H, m, ArH), 3.86 (3H, s, OCH$_3$), 3.85 (3H, s, OCH$_3$); $^{13}$C NMR (CDCl$_3$) δ: 161.8, 160.1, 141.6, 137.9, 127.8, 123.7, 113.6, 113.5, 55.6, 55.4; MS (ESI) 259 (M+Na$^+$, 100%).

1,2-Bis(3-methoxyphenyl)diazenec oxide (2j)

Yellow solid; mp 104-106 °C; 85% yield; $^1$H NMR (CDCl$_3$) δ: 7.92-7.71 (4H, m, ArH), 7.15-7.05 (1H, m, ArH), 6.99-6.93 (1H, m, ArH), 3.90 (3H, s, OCH$_3$), 3.87 (3H, s, OCH$_3$); $^{13}$C NMR (CDCl$_3$) δ: 159.8, 159.5, 149.4, 144.9, 129.4, 129.3, 118.3, 118.0, 116.3, 114.6, 110.0, 107.4, 55.6, 55.4; MS (ESI) 259 (M+H$,^+$, 100%).

1,2-Bis(4-phenoxyphenyl)diazenec oxide (2k)

Brown oil; 86% yield; $^1$H NMR (CDCl$_3$) δ: 8.34-8.16 (4H, m, ArH), 7.52-7.32 (4H, m, ArH), 7.17-6.95 (10H, m, ArH); $^{13}$C NMR (CDCl$_3$) δ: 160.2, 158.1, 156.0, 139.3, 130.0, 129.8, 127.7.
125.3, 124.4, 124.0, 123.9, 120.4, 119.8, 119.6, 117.7, 116.9, 116.6; HRMS exact mass calculated for \([M+\text{Na}]^+\) (C_{24}H_{18}N_{2}NaO_{3}) requires m/z 405.1210, found m/z 405.1211.

**1,2-Bis(4-(hexyloxy)phenyl)diazene oxide (2l)**

Brown oil; 84 % yield; \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 8.44-8.17 (4H, m, ArH), 7.13-6.87 (4H, m, ArH), 4.20-3.94 (4H, m, 2 x OCH\(_2\)), 1.93-1.68 (4H, m, 2 x CH\(_2\)), 1.44-1.32 (12H, m, 6 x CH\(_2\)), 1.01-0.75 (6H, m, 2 x CH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\): 161.4, 159.8, 141.4, 137.8, 127.8, 123.6, 114.1, 114.0, 68.4, 68.2, 31.5, 31.4, 29.1, 29.0, 25.6, 25.5, 22.6, 14.0; HRMS exact mass calculated for [M+Na]\(^+\) (C_{24}H_{34}N_{2}NaO_{3}) requires m/z 421.2462, found m/z 421.2465.

**1,2-Bis(4-nitrophenyl)diazene oxide (2m)**

Yellow solid; mp 190-191 °C; 65% yield; \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 8.54 (2H, dt, \(J = 9.4\) and 2.3 Hz, ArH), 8.41 (2H, dt, \(J = 9.4\) and 2.3 Hz, ArH), 8.36 (2H, dt, \(J = 9.5\) and 2.1 Hz, ArH), 8.28 (2H, dt, \(J = 9.5\) and 2.1 Hz, ArH); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\): 149.9, 147.7, 126.3, 124.5, 124.4, 123.8; MS (ESI) 288 (M\(^+\), 100%).
Reaction Optimization for the Organocatalytic Oxidation of Aniline 1a to Nitrobenzene 3a

![Reaction Scheme](image)

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General Procedure for the Organocatalytic Synthesis of Substituted Nitroarenes

Substituted aniline (1.00 mmol) was placed in a round bottom flask and dissolved in acetonitrile (2 mL). Aqueous buffer solution (1 mL, 0.6 M K$_2$CO$_3$ – 4 x 10$^{-4}$M EDTA disodium salt), acetonitrile (0.33 mL, 6.50 mmol) and 30% aqueous H$_2$O$_2$ (0.75 mL, 6.50 mmol) were added consecutively. The reaction mixture was left stirring for 1 hour at room temperature. The mixture was extracted with EtOAc (3 x 7 mL). All the organic layers were combined and dried over Na$_2$SO$_4$. The solvents were removed under vacuum and the product was isolated with enough purity (>95%) after filtration through a short silica plug (10% EtOAc in Pet. Ether). In case the product was not of sufficient purity, the crude product was purified using flash column chromatography to afford the desired product.

**Nitrobenzene (3a)$^6$**

Yellow liquid; 82% yield; $^1$H NMR (CDCl$_3$) $\delta$: 8.20 (2H, d, $J = 8.4$ Hz, ArH), 7.77-7.64 (1H, m, ArH), 7.60-7.46 (2H, m, ArH); $^{13}$C NMR (CDCl$_3$) $\delta$: 148.2, 134.5, 129.2, 123.4; MS (ESI) 123 (M+, 100%).

**1-Methoxy-2-nitrobenzene (3b)$^7$**

Yellow liquid; 84% yield; $^1$H NMR (CDCl$_3$) $\delta$: 7.80 (1H, dd, $J = 8.1$ and 1.7 Hz, ArH), 7.62-7.47 (1H, m, ArH), 7.17-6.93 (2H, m, ArH), 3.93 (3H, s, CH$_3$); $^{13}$C NMR (CDCl$_3$) $\delta$: 152.8, 139.5, 134.2, 125.5, 120.1, 113.4, 56.3; MS (ESI) 153 (M+, 100%).
1-Methoxy-3-nitrobenzene (3c)

![Chemical structure of 1-Methoxy-3-nitrobenzene (3c)](image)

Yellow oil; 89% yield; \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 7.81 (1H, dd, \(J = 8.2\) and 2.1 Hz, ArH), 7.71 (1H, t, \(J = 2.1\) Hz, ArH), 7.43 (1H, t, \(J = 8.2\) Hz, ArH), 7.22 (1H, dd, \(J = 8.2\) and 2.1 Hz, ArH), 3.88 (3H, s, CH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\): 160.0, 149.1, 129.9, 121.2, 115.7, 108.0, 55.7; MS (ESI) 153 (M+, 100%).

1-Methoxy-4-nitrobenzene (3d)

![Chemical structure of 1-Methoxy-4-nitrobenzene (3d)](image)

Colorless crystal; mp 74-76 °C; 87% yield; \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 8.21 (2H, d, \(J = 9.1\) Hz ArH), 6.96 (2H, d, \(J = 9.1\) Hz, ArH), 3.91 (3H, s, CH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\): 164.5, 141.4, 125.9, 114.0, 56.0; MS (ESI) 153 (M+, 100%).

1-Chloro-2-nitrobenzene (3e)

![Chemical structure of 1-Chloro-2-nitrobenzene (3e)](image)

Yellow solid; mp 30-31 °C; 78% yield; \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 7.86 (1H, d, \(J = 8.0\) Hz, ArH), 7.60-7.47 (2H, m, ArH), 7.45-7.30 (1H, m, ArH); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\): 147.9, 133.2, 131.9, 127.6, 127.0, 125.6; MS (ESI) 158 (M+, 100%).

2-Nitroaniline (3f)

![Chemical structure of 2-Nitroaniline (3f)](image)

Reaction time, 20 h; Orange solid; mp 69-71 °C; 86% yield; \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 8.05 (1H, d, \(J = 8.4\) Hz, ArH), 7.31 (1H, t, \(J = 8.4\) Hz, ArH), 6.80 (1H, d, \(J = 8.4\) Hz, ArH), 6.68-6.52 (1H, m,
ArH), 6.11 (2H, br s, NH₂); ¹³C NMR (CDCl₃) δ: 144.8, 135.6, 132.5, 125.8, 118.7, 116.6; MS (ESI) 137 (M-H⁺, 100%).

1-Methyl-3-nitrobenzene (3g)³

Yellow oil; 88% yield; ¹H NMR (CDCl₃) δ: 8.24-7.93 (2H, m, ArH), 7.57-7.28 (2H, m, ArH), 2.46 (3H, s, CH₃); ¹³C NMR (CDCl₃) δ: 148.2, 140.0, 135.6, 129.3, 124.0, 120.9, 21.2; MS (ESI) 137 (M+, 100%).

3-Nitrobenzoic acid (3h)¹¹

Reaction time, 20 h; quenched with HCl (1N, 10 mL) before extractions; Light yellow crystalline solid; mp 137-139 °C; 96% yield; ¹H NMR (DMSO) δ: 8.59 (1H, s, ArH), 8.45 (1H, d, J = 8.2 Hz, ArH), 8.31 (1H, d, J = 8.2 Hz, ArH), 7.78 (1H, t, J = 8.2 Hz, ArH); ¹³C NMR (DMSO) δ: 167.4, 147.8, 136.8, 135.7, 129.9, 125.9, 123.9; MS (ESI) 166 (M-H⁺, 100%).

4-Nitrobenzoic acid (3i)¹¹

Reaction time, 20 h; quenched with HCl (1N, 10 mL) before extractions; Light yellow crystalline solid; mp 240-242 °C; 89% yield; ¹H NMR (DMSO) δ: 8.17 (2H, d, J = 8.5 Hz, ArH), 8.03 (2H, d, J = 8.5 Hz, ArH); ¹³C NMR (DMSO) δ: 166.0, 149.9, 136.8, 130.7, 123.7; MS (ESI) 166 (M-H⁺, 100%).
1-Fluoro-4-nitrobenzene (3j) \(^6\)

\[
\begin{align*}
\text{Yellow liquid; 80% yield; } & \text{H NMR (CDCl}_3\text{) } \delta: 8.41-8.20 (2\text{H, m, ArH}), 7.37-7.02 (2\text{H, m, ArH}); \\
& \text{C NMR (CDCl}_3\text{) } \delta: 166.1 (d, J = 257.8 \text{ Hz}), 144.2, 126.2 (d, J = 10.0 \text{ Hz}) 116.3, (d, J = 23.7 \text{ Hz}); \\
& \text{F NMR (CDCl}_3\text{) } \delta: -22.7; \text{ MS (ESI) 142 (M+H}^+, 100\%).
\end{align*}
\]

2-(4-Nitrophenyl)acetic acid (3k) \(^{12}\)

\[
\begin{align*}
\text{Reaction time, 20 h; quenched with HCl (1N, 10 mL) before extractions; Yellow solid; mp 146-148 \text{ C; 88\% yield; } & \text{H NMR (DMSO) } \delta: 8.11 (2\text{H, d, } J = 8.1 \text{ Hz, ArH}), 7.49 (2\text{H, d, } J = 8.1 \text{ Hz, ArH}), 3.71 (2\text{H, s, CH}_2); \\
& \text{C NMR (DMSO) } \delta: 172.9, 146.3, 143.3, 130.9, 123.3, 40.8; \text{ MS (ESI) 180 (M-H}^-, 100\%).
\end{align*}
\]

2-Nitropyridine (3l) \(^{13}\)

\[
\begin{align*}
\text{Reaction time, 20 h; White solid; mp 66-68 \text{ C; 79\% yield; } & \text{H NMR (CDCl}_3\text{) } \delta: 8.69-8.48 (1\text{H, m, ArH}), 8.29-8.15 (1\text{H, m, ArH}), 8.12-7.97 (1\text{H, m, ArH}), 7.75-7.61 (1\text{H, m, ArH}); \\
& \text{C NMR (CDCl}_3\text{) } \delta: 156.4, 148.8, 140.0, 129.3, 117.9; \text{ MS (ESI) 125 (M+H}^+, 100\%).
\end{align*}
\]

1,3-Dinitrobenzene (3m) \(^{14}\)

\[
\begin{align*}
\text{Reaction time, 20 h; Yellow solid; mp 85-87 \text{ C; 74\% yield; } & \text{H NMR (CDCl}_3\text{) } \delta: 9.05 (1\text{H, t, } J = 2.2, \text{ ArH}), 8.58 (2\text{H, dd, } J = 8.2 \text{ and 2.2 Hz, ArH}), 7.86 (1\text{H, t, } J = 2.2, \text{ ArH}); \\
& \text{C NMR (CDCl}_3\text{) } \delta: 148.4, 130.8, 128.9, 119.0; \text{ MS (ESI) 168 (M+, 100\%).}
\end{align*}
\]
1,4-Dinitrobenzene (3n)$^{15}$

![Chemical Structure](image)

Reaction time, 20 h; Yellow solid; mp 169-171 °C; 65% yield; $^1$H NMR (CDCl$_3$) $\delta$: 8.41 (4H, s, ArH); $^{13}$C NMR (CDCl$_3$) $\delta$: 151.0, 124.8; MS (ESI) 168 (M+, 100%).
High Resolution Mass Spectrometry Studies

Instrumentation

The High Resolution Mass Spectra were recorded with a Q-TOF (Time of Flight Mass Spectrometry) Bruker Maxis Impact with ESI source and U-HPLC Thermo Dionex Ultimate 3000 pump and autosampler. N₂ was used as collision gas and electrospray ionization (ESI) – positive mode - was used for the MS experiments. The data acquisition was carried out with Data Analysis from Bruker Daltonics (version 4.1). For the MS experiments, a solution approximately of 10 mg/L in acetonitrile for each analyte was used. Acetonitrile LC-MS gradient was obtained from Carlo Erba Reagents (Chaussée du Vexin, France).

(Source conditions: End plate offset 500V, Capillary 4500V, Nebulizer 0.4 Bar, Dry gas 4.0 l/min, Dry temperature 180 °C and Quadrupole conditions: Ion energy 5 eV, Collision energy 10 eV, Transfer time 143 μs, Collision ion RF 3500 vpp, Pre pulse storage 1μs).

In this work, the mechanistic studies with High Resolution Mass Spectrometry under positive and negative mode are shown. It is widely recognized that high resolution and accuracy tandem mass spectrometry allows more reliable target analysis and screening of unknown compounds.¹⁶

Positive ESI mode

In Figure S1, the full scan High Resolution Mass Spectra of the reaction mixture at time: A) 0 min, B) 30 min, C) 60 min, D) 120 min, E) 180 min and F) 240 min are presented.
C)
Figure S1. Full scan High Resolution Mass Spectra of the reaction at time: A) 0 min, B) 30 min, C) 60 min, D) 120 min, E) 180 min and F) 240 min.
In Figure S2, the full scan High Resolution Mass Spectra of the reaction mixture at time: A) 0 min, B) 30 min, C) 60 min, D) 120 min, E) 180 min and F) 240 min are presented.
C) 

D)
Figure S2. Full scan High Resolution Mass Spectra of the reaction at time: A) 0 min, B) 30 min, C) 60 min, D) 120 min, E) 180 min and F) 240 min.
In Figure S3, the full scan High Resolution Mass Spectra of the reaction mixture at time: A) 0 min, B) 30 min, C) 60 min and D) 120 min are presented.
Figure S3. Full scan High Resolution Mass Spectra of the reaction at time: A) 0 min, B) 30 min, C) 60 min and D) 120 min.

**Positive ESI mode**

In Figure S4, the full scan High Resolution Mass Spectra of the reaction mixture at time: A) 0 min, B) 30 min, C) 60 min and D) 120 min are presented.

A)
Figure S4. Full scan High Resolution Mass Spectra of the reaction at time: A) 0 min, B) 30 min, C) 60 min and D) 120 min.
In Figure S5, the full scan High Resolution Mass Spectra of the reaction mixture at time:
A) 0 min, B) 30 min, C) 60 min and D) 120 min are presented.

A)
Figure S5. Full scan High Resolution Mass Spectra of the reaction at time: A) 0 min, B) 30 min, C) 60 min and D) 120 min.
In Figure S6, the full scan High Resolution Mass Spectra of the reaction mixture at time: A) 0 min, B) 30 min, C) 60 min and D) 120 min are presented.
Figure S6. Full scan High Resolution Mass Spectra of the reaction at time A) 0 min, B) 30 min, C) 60 min and D) 120 min.
Negative ESI mode

In Figure S7, the full scan High Resolution Mass Spectra of the reaction mixture at 30 min is presented.

A)

Figure S7. Full scan High Resolution Mass Spectra of the reaction at 30 min.
In Figure S8, the full scan High Resolution Mass Spectra of the reaction mixture at 30 min is presented.

Figure S8. Full Scan High Resolution Mass Spectra of the reaction at 30 min.
In Figure S9, the full scan High Resolution Mass Spectra of the reaction mixture at 30 min is presented.

Figure S9. Full scan High Resolution Mass Spectra of the reaction at 30 min.
Hammett Plot for the oxidation of Aniline to Azoxybenzene

Conversion of substituted aniline vs time

- ln(conversion) vs time
σ+ Hammett equation

σ Hammett equation
Hammett Plot for the oxidation of Aniline to Nitrobenzene

Conversion of substituted aniline vs time

- ln(conversion) vs time
σ+ Hammett equation

σ Hammett equation
References

E. Voutyritsa, A. Theodorou, M. G. Kokotou & C. G. Kokotos  Supporting Information S55
NO₂

3d