Supporting Information for

A practical route to azo compounds by metal-free aerobic oxidation of arylhydrazides using NO\textsubscript{x} system

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1. General Considerations

All commercially available compounds and solvents were purchased and used as received, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm) and treatment with phosphomolybdic acid stain followed by heating. Flash chromatography was performed using silica gel (particle size 40–63 \textmu m, 230–400 mesh). \textsuperscript{1}H, \textsuperscript{13}C, and \textsuperscript{19}F NMR spectra were recorded on 400 MHz NMR (400 MHz for \textsuperscript{1}H, 101 MHz for \textsuperscript{13}C, 376 MHz for \textsuperscript{19}F). Chemical shift values are given in parts per million relative to internal TMS (0.00 ppm for \textsuperscript{1}H) or CDCl\textsubscript{3} (77.06 ppm for \textsuperscript{13}C). The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d
= doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = double of doublet, dt = double of triplet, td = triple of doublet. Coupling constants, J, were reported in hertz unit (Hz). High-resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using FAB method and magnetic sector mass analyzer.

2. Preparation of hydrazides
All hydrazides were prepared according to the known procedures: 1a–f,[1] 1g,[2] 1h–n,[1] 1o,[3] 3a–l,[4] 5a–b,[5] and 5c.[6]

3. Optimization of metal-free aerobic oxidation of hydrazides
A 15 mm flame-dried test tube, which was equipped with a magnetic stir bar and charged with ethyl 2-phenylhydrazinecarboxylate (0.5 mmol) and NaNO₂ (10 mol %, 0.05 mmol), was evacuated and backfilled with oxygen (this process was repeated three times). After 0.5 mL of solvent was added, HNO₃ (20 mol %, 0.1 mmol) and solvent (0.5 mL) were added in sequence. After the time tested, the reaction was diluted by adding CH₂Cl₂ and washed with a saturated aqueous solution of Na₂CO₃. Two layers were separated, and the aqueous layer was extracted with CH₂Cl₂. The combined organic layer was dried over MgSO₄, filtered, and concentrated on rotary evaporator. The ¹H NMR yield of the desired product was determined by integration using an internal standard (1,1,2,2-tetrachloroethane).

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$^a$No NaNO$_2$. $^b$No HNO$_3$. $^c$The use of AcOH instead of HNO$_3$. $^d$The use of H$_2$SO$_4$ instead of HNO$_3$. $^e$The use of TsOH instead of HNO$_3$.

4. General procedure for NO$_x$-catalyzed aerobic oxidation of hydrazides

A 15 mm flame-dried test tube, which was equipped with a magnetic stir bar and charged with hydrazines (0.5 mmol) and NaNO$_2$ (10 mol %, 0.05 mmol), was evacuated and backfilled with oxygen (this process was repeated three times). After 0.5 mL of toluene was added, HNO$_3$ (20 mol %, 0.1 mmol) and toluene (0.5 mL) were added in sequence. The reaction mixture was stirred under an O$_2$ balloon at 50 °C for 3 h, and then cooled to room temperature. The reaction was diluted by adding CH$_2$Cl$_2$ and washed with a saturated aqueous solution of Na$_2$CO$_3$. Two layers were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$. The combined organic layer was dried over MgSO$_4$, filtered, and concentrated on rotary evaporator. The crude NMR of residue was pure, but, we purified the product by column chromatography for publication.

**Ethyl 2-phenylazocarboxylate$^{[b]}$ (2a); 99% (88.2 mg), orange oil, EA/hexane = 1:5. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 (d, J=8.3 Hz, 2H), δ 7.59-7.50 (m, 3H), δ 4.51 (q, J=7.1 Hz, 2H), δ 1.46 (t, J=7.1 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.2, 151.6, 133.8, 129.3, 123.7, 64.5, 14.2.**
Ethyl 2-(4-methoxyphenyl)azocarboxylate\(^{[3]}\) (2b); 97% (101.0 mg), red oil, EA/hexane = 1:5, \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 (d, J=9.1 Hz, 2H), \(\delta\) 7.00 (d, J=9.1 Hz, 2H), \(\delta\) 4.50 (q, J=7.1 Hz, 2H), \(\delta\) 3.90 (s, 3H), \(\delta\) 1.46 (t, J=7.1 Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 164.6, 162.1, 146.1, 126.4, 114.4, 64.1, 55.7, 14.2.

Ethyl 2-(4-methylphenyl)azocarboxylate\(^{[3]}\) (2c); 99% (95.1 mg), orange oil, EA/hexane = 1:5, \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, J=8.3 Hz, 2H), \(\delta\) 7.32 (d, J=8.0 Hz, 2H), \(\delta\) 4.51 (q, J=7.1 Hz, 2H), \(\delta\) 2.44 (s, 3H), \(\delta\) 1.47 (t, J=7.1 Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.2, 149.8, 145.1, 130.0, 123.9, 64.3, 21.7, 14.2.

Ethyl 2-(4-bromophenyl)azocarboxylate\(^{[3]}\) (2d); 98% (126.0 mg), orange oil, EA/hexane = 1:5, \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, J=8.8 Hz, 2H), \(\delta\) 7.72 (d, J=8.7 Hz, 2H), \(\delta\) 4.57 (q, J=7.1 Hz, 2H), \(\delta\) 1.52 (t, J=7.1 Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 161.9, 150.2, 132.7, 128.8, 125.1, 64.6, 14.1.

Ethyl 2-(4-chlorophenyl)azocarboxylate\(^{[3]}\) (2e); 99% (105.3 mg), orange oil, EA/hexane = 1:5, \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.88 (d, J=8.8 Hz, 2H), \(\delta\) 7.50 (d, J=8.8 Hz, 2H), \(\delta\) 4.52 (q, J=7.1 Hz, 2H), \(\delta\) 1.47 (t, J=7.1 Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 161.9, 149.9, 140.1, 129.6, 125.0, 64.6, 14.1.

Ethyl 2-(4-fluorophenyl)azocarboxylate\(^{[3]}\) (2f); 98% (96.1 mg), orange oil, EA/hexane = 1:5, \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.01-7.94 (m, 2H), \(\delta\) 7.21 (t, J=8.5 Hz, 2H), \(\delta\) 4.52 (q, J=7.1 Hz, 2H), \(\delta\) 1.47 (t, J=7.1 Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.0 (d, J= 256.6 Hz), 148.1 (d, J= 3.0 Hz), 126.1 (d, J=9.6 Hz), 116.4 (d, J=23.2 Hz), 64.5, 14.1; \(^{19}\)F NMR (376MHz, CDCl\(_3\)) \(\delta\) -104.2.

Ethyl 2-[4-(ethoxycarbonyl)phenyl]azocarboxylate\(^{[2]}\) (2g); 99% (123.9 mg), orange oil, EA/hexane
= 1:5, $^1$H NMR (400 MHz, CDCl$_3$) δ 8.21 (d, J=8.5 Hz, 2H), δ 7.96 (d, J=8.5 Hz, 2H), δ 4.54 (q, J=7.1 Hz, 2H), δ 4.42 (q, J=7.1 Hz, 2H), δ 1.48 (t, J=7.1 Hz, 3H), δ 1.42 (t, J=7.1 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.4, 161.9, 153.8, 134.6, 130.6, 123.4, 64.7, 61.5, 14.3, 14.2.

**Ethyl 2-(4-cyanophenyl)azocarboxylate**[3] (2h); 99% (100.6 mg), orange oil, EA/hexane = 1:5, $^1$H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, J=8.4 Hz, 2H), δ 7.84 (d, J=8.3 Hz, 2H), δ 4.54 (q, J=7.1 Hz, 2H), δ 1.48 (t, J=7.1 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.6, 153.1, 133.4, 123.9, 117.7, 116.7, 65.0, 14.1.

**Ethyl 2-(4-nitrophenyl)azocarboxylate**[3] (2i); 97% (108.2 mg), red solid, EA/hexane = 1:5, $^1$H NMR (400 MHz, CDCl$_3$) δ 8.40 (d, J=9.1 Hz, 2H), δ 8.06 (d, J=9.1 Hz, 2H), δ 4.56 (q, J=7.1 Hz, 2H), δ 1.49 (t, J=7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.5, 154.2, 150.3, 124.8, 124.2, 65.0, 14.1.

**Ethyl 2-(2-chlorophenyl)azocarboxylate**[3] (2j); 75% (79.7 mg), orange oil, EA/hexane = 1:5, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64-7.55 (m, 2H), δ 7.49 (t, J=7.0 Hz, 1H), δ 7.33 (t, J=7.1 Hz, 1H), δ 4.52 (q, J=7.1 Hz, 2H), δ 1.46 (t, J=7.1 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.0, 147.9, 137.3, 134.4, 131.1, 127.3, 117.2, 64.6, 14.1.

**Ethyl 2-(3,4-dichlorophenyl)azocarboxylate**[3] (2k); 99% (122.3 mg), red solid, EA/hexane = 1:5, $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (s, 1H), δ 7.80 (d, J=8.5 Hz, 1H), δ 7.63 (d, J=8.5 Hz, 1H), δ 4.53 (q, J=7.1 Hz, 2H), δ 1.47 (t, J=7.1 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.6, 150.3, 138.1, 134.0, 131.2, 124.6, 123.5, 64.8, 14.2.

**Ethyl 2-(3,5-dichlorophenyl)azocarboxylate**[3] (2l); 98% (121.1 mg), orange oil, EA/hexane = 1:5,
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 (s, 2H), \(\delta\) 7.56 (s, 1H), \(\delta\) 4.53 (q, \(J=7.1\) Hz, 2H), \(\delta\) 1.47 (t, \(J=7.1\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 161.5, 152.4, 136.0, 132.9, 122.1, 64.8, 14.1.

**Ethyl 2-(2,3,4,5,6-pentafluorophenyl)azocarboxylate\(^{[3]}\) (2m);** 92% (123.3 mg), orange oil, EA/hexane = 1:5, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.54 (q, \(J=7.1\) Hz, 2H), \(\delta\) 1.48 (t, \(J=7.1\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 160.7, 144.8-144.6 (m), 144.3-143.0 (m), 142.4-142.0 (m), 140.7-140.3 (m), 139.5-139.0 (m), 136.9-136.5 (m), 126.9-126.7 (m), 65.2, 14.0; \(^{19}\)F NMR (376MHz, CDCl\(_3\)) \(\delta\) -146.5, -160.9.

\[\text{Ethyl 2-(2,3,4,5,6-pentafluorophenyl)azocarboxylate}\]

\[\begin{align*}
&\text{F} & &\text{F} \\
&\text{F} & &\text{F} \\
&\text{F} & &\text{F} \\
&\text{F} & &\text{F} \\
&\text{N} & &\text{N} \\
&\text{O} & &\text{Et}
\end{align*}\]

**2,2,2-Trichloroethyl 2-phenylazocarboxylate\(^{[3]}\) (2n);** 99% (139.4 mg), orange oil, EA/hexane = 1:5, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.99 (d, \(J=7.7\) Hz, 2H), \(\delta\) 7.64 (t, \(J=7.3\) Hz, 1H), \(\delta\) 7.56 (t, \(J=7.5\) Hz, 2H), \(\delta\) 5.07 (s, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 160.7, 151.7, 134.6, 129.4, 124.2, 94.0, 76.5.

\[\text{2,2,2-Trichloroethyl 2-phenylazocarboxylate}\]

\[\begin{align*}
&\text{Cl} \\
&\text{Cl} \\
&\text{Cl} \\
&\text{O} & &\text{O} \\
&\text{C} & &\text{C} \\
&\text{N} & &\text{N}
\end{align*}\]

**Benzyl 2-phenylazocarboxylate\(^{[3]}\) (2o);** 97% (116.5 mg), orange oil, EA/hexane = 1:5, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92 (d, \(J=7.6\) Hz, 2H), \(\delta\) 7.60-7.56 (m, 1H), \(\delta\) 7.54-7.45 (m, 4H), \(\delta\) 7.43-7.36 (m, 3H), \(\delta\) 5.47 (s, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.1, 151.6, 134.4, 133.9, 129.3, 128.9, 128.8, 128.7, 123.8, 69.9.

\[\text{Benzyl 2-phenylazocarboxylate}\]

\[\begin{align*}
&\text{N} & &\text{O} \\
&\text{N} & &\text{O} \\
&\text{C} & &\text{C} \\
&\text{Me} & &\text{O}
\end{align*}\]

**Benzoylazobenzene\(^{[3]}\) (4a);** 99% (104.1 mg), red oil, EA/hexane = 1:5, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.06 (d, \(J=8.1\) Hz, 2H), \(\delta\) 8.00 (d, \(J=7.9\) Hz, 2H), \(\delta\) 7.66 (t, \(J=7.4\) Hz, 1H), \(\delta\) 7.62-7.49 (m, 5H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 182.0, 152.0, 134.6, 133.4, 130.8, 130.5, 129.4, 128.9, 128.7, 123.6.

\[\text{Benzoylazobenzene}\]

\[\begin{align*}
&\text{N} & &\text{O} \\
&\text{N} & &\text{O} \\
&\text{C} & &\text{C} \\
&\text{Me} & &\text{O}
\end{align*}\]

**Benzoyl-2-(4-methoxyphenyl)diazene\(^{[7]}\) (4b);** 98% (117.7 mg), dark red oil, EA/hexane = 1:5, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.11 (d, \(J=7.5\) Hz, 2H), \(\delta\) 8.01 (d, \(J=8.9\) Hz, 2H), \(\delta\) 7.64 (t, \(J=7.4\) Hz, 1H),
$\delta$ 7.51 (t, J=7.7 Hz, 2H), $\delta$ 7.03 (d, J=8.9 Hz, 2H), $\delta$ 3.90 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 181.5, 164.2, 146.8, 134.3, 131.7, 130.6, 128.8, 126.2, 114.5, 55.8.

**Benzoyl-2-(4-methylphenyl)diazene**$^{[7]}$ (4c); 99% (111.0 mg), orange solid, EA/hexane = 1:5, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (d, J=7.8 Hz, 2H), $\delta$ 7.90 (d, J=8.2 Hz, 2H), $\delta$ 7.63 (t, J=7.4 Hz, 1H), $\delta$ 7.49 (t, J=7.7 Hz, 2H), $\delta$ 7.34 (d, J=8.1 Hz, 2H), $\delta$ 2.44 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 181.9, 150.4, 144.6, 134.4, 131.1, 130.5, 130.0, 128.8, 123.7, 21.7.

**Benzoyl-2-(4-bromophenyl)diazene**$^{[7]}$ (4d); 99% (143.1 mg), orange solid, EA/hexane = 1:5, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, J=8.3 Hz, 2H), $\delta$ 7.87 (d, J=8.6 Hz, 2H), $\delta$ 7.73-7.65 (m, 3H), $\delta$ 7.53 (t, J=7.7 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 181.6, 150.7, 134.7, 132.7, 130.7, 130.5, 128.9, 128.4, 125.0.

**Benzoyl-2-(4-fluorophenyl)diazene**$^{[8]}$ (4e); 97% (110.7 mg), red solid, EA/hexane = 1:5, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10-7.98 (m, 4H), $\delta$ 7.66 (t, J=7.4 Hz, 1H), $\delta$ 7.52 (t, J=7.7 Hz, 2H), $\delta$ 7.24 (t, J=8.4 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 181.6, 165.8 (d, J=255.9 Hz), 148.6 (d, J=2.8 Hz), 134.6, 130.8, 129.7 (d, J=165.5 Hz), 123.0 (J=9.5 Hz), 116.5(J=23.2 Hz); $^{19}$F NMR (376MHz, CDCl$_3$) $\delta$ -104.2.

**Benzoyl-2-(4-cyanophenyl)diazene**$^{[8]}$ (4f); 99% (116.4 mg), light brown solid, EA/hexane = 1:5, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (d, J=8.4 Hz, 2H), $\delta$ 8.02 (d, J=8.2 Hz, 2H), $\delta$ 7.88 (d, J=8.4 Hz, 2H), $\delta$ 7.70 (t, J=7.4 Hz, 1H), $\delta$ 7.55 (t, J=7.7 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 181.4, 153.5, 135.0, 133.5, 130.5, 130.1, 129.1, 123.9, 117.9, 116.4.

**Benzoyl-2-(4-nitrophenyl)diazene**$^{[7]}$ (4g); 98% (125.1 mg), orange solid, EA/hexane = 1:5, $^1$H
NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 (d, $J$=8.9 Hz, 2H), $\delta$ 8.12 (d, $J$=8.9 Hz, 2H), $\delta$ 8.03 (d, $J$= 7.3Hz, 2H), $\delta$ 7.71 (t, $J$=7.4 Hz, 1H), $\delta$ 7.56 (t, $J$=7.7 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 181.3, 154.5, 150.1, 135.0, 130.5, 130.0, 129.1, 124.9, 124.1.

![Image](image_url)

(4-Methylbenzoyl)-2-phenyldiazene$^{[8]}$ (4h); 99% (111.0 mg), orange solid, EA/hexane = 1:5, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01-7.92 (m, 4H), $\delta$ 7.61-7.52 (m, 3H), $\delta$ 7.30 (d, $J$=8.2 Hz, 2H), $\delta$ 2.43 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 181.9, 152.1, 145.7, 133.3, 130.6, 129.6, 129.3, 128.2, 123.5, 21.9.

![Image](image_url)

(2-Chlorobenzoyl)-2-phenyldiazene (4i); 99% (121.1 mg), red oil, EA/hexane = 1:5, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02-7.94 (m, 3H), $\delta$ 7.61-7.52 (m, 5H), $\delta$ 7.44-7.37 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 181.5, 152.1, 134.7, 134.1, 133.6, 132.9, 131.5, 130.9, 126.9, 123.8; HRMS (FAB) m/z calcd. for C$_{13}$H$_{10}$ClN$_2$O$_1$ [M + H]$^+$: 245.0482, found 245.0484.

![Image](image_url)

(3-Chlorobenzoyl)-2-phenyldiazene (4j); 97% (118.7 mg), red solid, EA/hexane = 1:5, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.06 (s, 1H), $\delta$ 8.01 (d, $J$=6.8 Hz, 2H), $\delta$ 7.96 (d, $J$=7.4 Hz, 1H), $\delta$ 7.66-7.55 (m, 4H), $\delta$ 7.48 (t, $J$=7.9 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.5, 152.0, 135.1, 134.4, 133.8, 132.6, 130.4, 130.2, 129.4, 128.6, 123.7; HRMS (FAB) m/z calcd. for C$_{13}$H$_{10}$ClN$_2$O$_1$ [M + H]$^+$: 245.0482, found 245.0485.

![Image](image_url)

(4-Chlorobenzoyl)-2-phenyldiazene$^{[8]}$ (4k); 98% (119.9 mg), red solid, EA/hexane = 1:5, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04-7.98 (m, 4H), $\delta$ 7.64-7.54 (m, 3H), $\delta$ 7.50 (d, $J$=8.6 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.7, 152.0, 141.2, 133.7, 131.9, 129.4(2C), 129.3, 123.7.

![Image](image_url)

Diethyl azodicarboxylate$^{[5]}$ (6a); crude yield: 76% (66.2 mg), EA/hexane = 1:5, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.51 (q, $J$=7.1 Hz, 4H), $\delta$ 1.45 (t, $J$=7.1 Hz, 6H).
Diisopropyl azodicarboxylate<sup>[5]</sup> (6b); 77% (77.9 mg), yellow oil, EA/hexane = 1:5, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.29-5.19 (m, 2H), δ 1.43 (d, J=6.3 Hz, 12H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.0, 74.4, 21.6.

Diazobenzene<sup>[6]</sup> (6c); 99% (90.2 mg), orange solid, EA/hexane = 1:20, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (d, J=7.0 Hz, 4H), δ 7.55-7.44 (m, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.7, 131.0, 129.1, 122.9.

5. Procedure for NO<sub>x</sub>-catalyzed aerobic oxidation of hydrazide on large scale

A 250 mL round-bottom flask, which was equipped with a magnetic stir bar and charged with ethyl 2-(4-nitrophenyl)hydrazinecarboxylate (40 mmol) and NaNO<sub>2</sub> (10 mol %, 4 mmol), was evacuated and backfilled with oxygen (this process was repeated three times). After 50 mL of toluene was added, HNO<sub>3</sub> (20 mol %, 8 mmol) and toluene (50 mL) were added in sequence. The reaction mixture was stirred under an O<sub>2</sub> balloon at 50 °C for 4 h, and then cooled to room temperature. The reaction was diluted by adding CH<sub>2</sub>Cl<sub>2</sub> and washed with a saturated aqueous solution of Na<sub>2</sub>CO<sub>3</sub>. The combined organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated on rotary evaporator. The residue was pure without further purification. The crude NMR was attached below.
6. Procedure for the one-pot annulation reaction

A 15 mm flame-dried test tube, which was equipped with a magnetic stir bar and charged with 1-benzoyl-2-phenylhydrazine (0.75 mmol) and NaNO\textsubscript{2} (10 mol %, 0.075 mmol), was evacuated and backfilled with oxygen (this process was repeated three times). After 0.75 mL of CH\textsubscript{3}CN was added, HNO\textsubscript{3} (20 mol %, 0.15 mmol) and CH\textsubscript{3}CN (0.75 mL) were added in sequence. The reaction mixture was stirred under an O\textsubscript{2} balloon at 50 °C. After 3 h, the reaction mixture was added to 100 mL two neck round bottom flask, which was equipped with a magnetic stir bar, K\textsubscript{2}CO\textsubscript{3} (3 mmol, 414.6 mg), CH\textsubscript{3}CN (2.5 mL), and reflux system under N\textsubscript{2}. Then, the test tube was washed with the additional CH\textsubscript{3}CN (1 mL) and the solution was added to the round bottom flask. After the addition of PhNCS (0.5 mmol, 62 µL) to the round bottom flask, the reaction mixture was refluxed. After 2 h, the reaction mixture was cooled, quenched with 5% Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (5 mL), diluted with brine (10 mL), and then extracted with EtOAc (15 mL × 3). The combined organic layer was dried over MgSO\textsubscript{4}, filtered, and concentrated on rotary evaporator. The residue was purified by column chromatography to give annulation product (EtOAc/PE=1:60).

\[(Z)-N,3,5-Triphenyl-1,3,4-oxadiazol-2(3H)-imine\textsuperscript{[9]} (7a); 83% (130.0 mg), white solid, EA/PE = 1:60, \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.22 (d, J=7.8 Hz, 2H), δ 7.89 (d, J=7.9 Hz, 2H), δ 7.52-7.42 (m, 5H), δ 7.40-7.29 (m, 4H), δ 7.21 (t, J=7.4 Hz, 1H), δ 7.10 (t, J=7.1 Hz, 1H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 152.8, 145.5, 144.4, 137.6, 131.5, 129.0, 128.9(2C), 125.9, 124.9, 123.6, 123.3, 123.2, 118.5.

7. References

8. $^1$H, $^{13}$C and $^{19}$F NMR spectra of substrates

Ethyl 2-phenylazocarboxylate (2a)
Ethyl 2-(4-methoxyphenyl)azocarboxylate (2b)
Ethyl 2-(4-methylphenyl)azocarboxylate (2c)
Ethyl 2-(4-bromophenyl)azocarboxylate (2d)
Ethyl 2-(4-chlorophenyl)azocarboxylate (2e)
Ethyl 2-(4-fluorophenyl)azocarboxylate (2f)
Ethyl 2-[4-(ethoxycarbonyl)phenyl]azocarboxylate (2g)
Ethyl 2-(4-cyanophenyl)azocarboxylate (2h)
Ethyl 2-(4-nitrophenyl)azocarboxylate (2i)
Ethyl 2-(2-chlorophenyl)azocarboxylate (2j)
Ethyl 2-(3,4-dichlorophenyl)azocarboxylate (2k)
Ethyl 2-(3,5-dichlorophenyl)azocarboxylate (2I)
Ethyl 2-(2,3,4,5,6-pentafluorophenyl)azocarboxylate (2m)
2,2,2-Trichloroethyl 2-phenylazocarboxylate (2n)
Benzyl 2-phenylazocarboxylate (2o)
Benzoylazobenzene (4a)
Benzoyl-2-(4-methoxyphenyl)diazene (4b)
Benzoyl-2-(4-methylphenyl)diazene (4c)
Benzoyl-2-(4-bromophenyl)diazene (4d)
Benzoyl-2-(4-fluorophenyl)diazene (4e)
Benzoyl-2-(4-cyanophenyl)diazene (4f)
Benzoyl-2-(4-nitrophenyl)diazene (4g)
(4-Methylbenzoyl)-2-phenyldiazene (4h)
(2-Chlorobenzoyl)-2-phenyldiazene (4i)
(3-Chlorobenzoyl)-2-phenyldiazene (4j)
(4-Chlorobenzoyl)-2-phenyldiazene (4k)
Diethyl azodicarboxylate (6a)
Diisopropyl azodicarboxylate (6b)
Diazobenzene (6c)
(Z)-N,3,5-Triphenyl-1,3,4-oxadiazol-2(3H)-imine (7a)