Autoinductive Conversion of $\alpha,\alpha$-Diiodonitroalkanes to Amides and Esters Catalysed by Iodine Byproducts under $O_2$

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1. General Information

Glassware was oven-dried at 120 °C for all non-aqueous reactions. All reagents and solvents were commercial grade and purified prior to use when necessary. Acetonitrile (CH$_3$CN), ether, and tetrahydrofuran (THF) were dried by passage through a column of activated alumina. Analytical thin-layer chromatography (TLC) was performed using E. Merck Silica gel 60 F254 pre-coated plates. Column chromatography was performed using 40–50 μm Silica Gel 60N (Kanto Chemical Co., Inc.). $^1$H-NMR (400 MHz) and $^{13}$C-NMR (100 MHz) spectra were recorded on an Agilent 400MR spectrometer. Chemical shifts are reported in (ppm) down field from tetramethylsilane with reference to solvent signals [$^1$H NMR: CHCl$_3$ (7.26); $^{13}$C NMR: CDCl$_3$ (77.0)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak; coupling constants are given in (Hz). Infrared (IR) spectra were recorded on a PERKIN ELMER Spectrum BX FT-IR System spectrometer. High resolution mass spectra were measured on a Thermo Fisher Scientific Orbitrap Discovery (ESI LTQ Orbitrap).

React IR Information: React IR 15, Probe A: ReactIR 15 (SN: unspecified) with MCT Detector using HappGenzel apodization; DiComp (Diamond) probe (SN: unspecified) connected via AgX 6mm 1.5m Fiber (Silver Halide); Sampling 2500 to 650 at 8 wavenumber resolution; Scan option: AutoSelect; Gain: 1.
2. Preparation of starting materials

**Scheme S-1.** Preparation of α,α-diiodonitroalkane 2a.

**Synthesis of nitroalkane 1a:** The iodide S-1 was dissolved in dry Et2O (50 mL) and AgNO2 was added in one-portion. The reaction mixture was stirred at r.t. until all the iodide S-1 was consumed, after which the reaction was filtered and concentrated under reduced pressure to afford the crude compound 1a, which was columned via silica gel chromatography (Hex/EA = 10/1) to give pure 1a (62.5%) as a colorless sticky oil.

\[
\text{Ph}\text{CH}_2\text{CH}_2\text{I} + \text{AgNO}_2 \xrightarrow{\text{Et}_2\text{O}} \text{Ph}\text{CH}_2\text{CH}_2\text{NO}_2 + \text{AgI}
\]

\[
\begin{align*}
\text{1a (25 mmol)} \quad &\xrightarrow{\text{K}_2\text{CO}_3 (2 \text{eq.})} \quad \text{MeOH (0.5 M)} \\
&\quad 0 \degree \text{C, 10 min} \quad \text{Ph}\text{-CH}_2\text{CH}_2\text{NO}_2 \quad \text{K}^+ \quad 0 \degree \text{C} \\
&\quad 10 \text{ min} \quad \text{Ph}\text{-CH}_2\text{CH}_2\text{I}
\end{align*}
\]

\[
\text{IR (neat): 2929, 1552, 1383, 701 cm}^{-1}
\]

\[
\text{HRMS (ESI): m/z calcd. for C}_9\text{H}_{11}\text{NNaO}_2 (M + Na)^+ 188.0682; found: 188.0885.}
\]

**Synthesis of α,α-diiodonitroalkane 2a:** Nitroalkane 1a (25 mmol) was dissolved in methanol (50 mL) in a two necked flask. The flask was degassed using freeze-pump-thaw techniques and back-filled with nitrogen (3 cycles). Next, K2CO3 (2.0 equiv.) was added in one portion at 0 °C and the reaction stirred for 10 min. The reaction was then cooled to -30 °C and I2 (2.0 eq.) was added at the same reaction temperature. After stirring for 10 min, the mixture was quenched with
NH₄Cl (400 mL) and extracted with pre-cooled CH₂Cl₂ (-30 °C, 150 × 2mL). The organic phase was dried over MgSO₄ at -30 °C, then quickly filtered and concentrated in vacuo over an ice bath to afford a yellow crude solid. The crude product was purified sequentially 3 times via recrystallization (CH₂Cl₂ + hexane) at -30 °C to afford yellow crystals of 2a (yield = 40 %). The crystal solid was further purified by grinding and washing with cold hexane (five times) to obtain pure 2a as a microcrystalline powder. In this solid state, 2a can be stored at -30 °C for up to 6 months without any decomposition and stored at r.t. for at least 3 days.

Caution: Employing highly pure α,α-diiodonitroalkane 2a is key to obtaining accurate kinetic profiles for oxidative reactions. If the crystals are purple-red, the induction times become very short, presumably due to iodine-based impurities.

**Scheme S-2.** Preparation of nitroalkane 12a/12b.
**Synthesis of S-2:** To a 100 mL flask containing the ketone (40 mmol) and MeNO₂ (200 mmol) was added a saturated methanolic solution of NH₃ (20 mL) and the reaction was stirred at r.t. under an NH₃ atmosphere (NH₃ balloon). After stirring overnight, all the volatile compounds were removed *in vacuo* to give the crude product S-2, which was used for the next step without purification.

**Synthesis of 12a and 12b:** Crude S-2 was dissolved in CH₂Cl₂ (50 mL) and cooled to 0 °C, CbzCl (20 mmol) and NEt₃ (20 mmol) were added. After stirring at r.t. for 3 h, the reaction mixture was quenched with sat. NaHCO₃ solution and extracted with CHCl₃. The combined organic solution was dried over anhydrous magnesium sulfate, the solvent was removed *in vacuo* and the give crude product was columned by silica gel chromatography (Hexane/ Ethyl Acetate = 3/1) to give pure 12a or 12b.

![Diagram of 12a](image)

White solid, yield = 80% (over 2 steps)

**¹H NMR** (400 MHz, CDCl₃): δ 1.42 (s, 6H), 4.73 (s, 2H), 4.89 (br s, 1H), 5.09 (s, 2H), 7.30-7.35 (s, 5H).

**¹³C NMR** (100 MHz, CDCl₃): δ 25.56, 52.25, 66.63, 80.78, 127.97, 128.20, 128.56, 136.12, 154.64.

**IR** (neat): 2982, 1716, 1550, 1250, 1090 cm⁻¹.

**HRMS** (ESI): *m/z* calcd. for C₁₂H₁₆N₂NaO₄ (M + Na)⁺ 275.1002; found: 275.1400.

![Diagram of 12b](image)
Sticky oil, yield = 70% (over steps)

**H NMR** (400 MHz, CDCl\(_3\)): \(\delta\) 1.28-1.31 (m, 1H), 1.46-1.63 (m, 8H), 2.02-2.05 (m, 2H), 4.67 (br s, 1H), 4.77 (s, 2H), 5.10 (s, 2H), 7.29-7.37 (m, 5H).

**C NMR** (100 MHz, CDCl\(_3\)): \(\delta\) 20.95, 25.07, 32.90, 54.62, 66.60, 80.21, 127.91, 128.17, 128.56, 136.20, 154.64, 154.64.

**IR** (neat): 3342, 2937, 1717, 1547, 1253, 1221 cm\(^{-1}\).

**HRMS** (ESI): \(m/z\) calcd. for C\(_{15}\)H\(_{20}\)N\(_2\)O\(_4\) (M + Na)\(^+\) 315.1315; found: 315.1318.

**Scheme S-3.** Preparation of \(\alpha,\alpha\)-diiodonitroalkane 12c.

**Step 1:** In a 200 mL flask, MeNO\(_2\) (50 mmol) and ketone (10 mmol) were dissolved in MeOH (50 mL). The reaction mixture was cooled to 0 °C, after which NaOH solution (50 mmol in 20 mL water) was added slowly and the reaction was stirred at the same temperature until the ketone disappeared by TLC analysis. The reaction mixture was then diluted with water, slowly neutralized with 1M HCl solution, and extracted with CHCl\(_3\). The combined organic solution was dried over anhydrous magnesium sulfate, the solvent removed in vacuo, and the crude product was columned by silica gel chromatography to give pure S-3.

**Step 2:** Pure S-3 was dissolved in CHCl\(_3\) (0.1 M), CH\(_2\)(OMe)\(_2\) (15 equiv.) was added in one portion, and P\(_2\)O\(_5\) powder was added slowly until S-3 was consumed. The reaction was then diluted with CHCl\(_3\) and filtered through a short silica gel column to remove precipitate and the solution collected was evaporated in vacuo to afford the pure product 12c quantitatively.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.56-1.66 (m, 2H), 1.76-1.99 (m, 3H), 2.12-2.20 (m, 2H), 2.47-2.54 (m, 2H), 3.47 (s, 3H), 4.55 (s, 2H), 4.83 (s, 2H), 7.17-7.31 (m, 5H).

$^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ 28.51, 32.93, 33.95, 41.35, 43.06, 56.42, 75.09, 83.15, 91.34, 126.23, 126.71, 128.43, 146.26.

IR (neat): 2360, 1550, 1024, 1141 cm$^{-1}$.

HRMS (ESI): $m/z$ calcd. for C$_{15}$H$_{21}$NNaO$_4$ (M + Na)$^+$ 302.1363; found: 302.1366.

Scheme S-4. Preparation of nitroalkane 12d/12e.

**Step 1:**$^{[1]}$ α,β-Unsaturated acid$^{[2]}$ (10 mmol), CuCl (1 mmol) and tertiary butyl nitrite (20 mmol) and CH$_3$CN (40 mL) were added to an oven dried round bottom flask. The reaction mixture was stirred at 80 °C. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure, and the crude product was purified on silica gel column to afford the pure nitroalkene S-4.

**Step 2:** To a solution of S-4 (5.0 mmol) in 20 ml of anhydrous Et$_2$O at −20 °C under Ar, was added the Grignard reagent (1 equiv.) in diethylether dropwise. The mixture was stirred at −20
°C for 20 min, warmed to R.T. over 2 h, and then poured onto excess ice. The mixture was made slightly acidic with 1M HCl solution. The aqueous layer was extracted once with ether. The combined organic layers were washed twice with water, made slightly acidic with dilute hydrochloric acid, and washed twice with saturated sodium chloride solution. Products 12d and 12e were isolated after drying with anhydrous magnesium sulfate, solvent removal and column purification (Hexane/EA= 1/5).

\[ \text{12d} \]

Sticky oil, 70%

\[ ^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3): \delta \ 1.96 \ (s, 3H), 5.10 \ (s, 2H), 7.16-7.34 \ (m, 10H). \]

\[ ^{13}C \text{ NMR} \ (100 \text{ MHz, CDCl}_3): \delta \ 25.56, 52.25, 66.63, 80.78, 127.97, 128.20, 128.56, 136.12, 154.64. \]

\[ ^\text{IR} \ (\text{neat}): \ 2616, 1552, 699 \text{ cm}^{-1}. \]

\[ ^\text{HRMS} \ (\text{ESI}): \ m/z \ \text{calcd. for C}_{15}\text{H}_{15}\text{NaO}_2 \ (\text{M} + \text{Na})^+ 264.0995; \text{ found: 264.0992.} \]

\[ \text{12e} \]

White solid, 80%

\[ ^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3): \delta \ 3.77 \ (s, 2H), 5.05 \ (s, 2H), 6.74 \ (d, J = 7.2 \text{ Hz, 2H}), 7.03-7.32 \ (m, 13H). \]

\[ ^{13}C \text{ NMR} \ (400 \text{ MHz, CDCl}_3): \delta \ 42.60, 51.48, 80.95, 126.80, 127.23, 127.83, 127.96, 128.31, 131.07, 136.04, 143.73. \]

\[ ^\text{IR} \ (\text{neat}): \ 3024, 1550, 1493, 1447, 1376, 755, 698 \text{ cm}^{-1}. \]
HRMS (ESI): \( m/z \) calcd. for \( \text{C}_{21}\text{H}_{19}\text{NaN}_2 \) (M+Na)\(^+\) 340.1308; found 340.1304.

Scheme S-5. Preparation of nitroalkane 12f/12g.

**Step 1:**\(^{[3]}\) To an oven-dried screw-capped test-tube charged with a magnetic stir-bar was added AgNO\(_2\) (3 equiv.), TEMPO (0.4 equiv.), olefin and oven-dried molecular sieves (4 Å, 150 mg). The olefin (20 mmol) and solvent (DCE, 0.04 M) were added by microliter syringe and laboratory syringe respectively. The tube was placed in a preheated oil bath at 70 °C and the reaction mixture was stirred vigorously for 12h. After the reaction mixture cooled to room temperature, the reaction was filtered through a celite bed filter with ethyl acetate as the washing solvent. The organic extract was concentrated and the product S-5 purified by column chromatography using silica gel and Hexane / ethyl acetate as the eluent.

**Step 2:** To a solution of S-5 (5.0 mmol) in 20 ml of anhydrous Et\(_2\)O at –20 °C under Ar, was added the Grignard reagent (1 equiv.) in diethylether dropwise. The mixture was stirred at –20 °C for 20 min, warmed to R.T. over 2 hr, and then poured onto excess ice. The mixture was made slightly acidic with 1M HCl solution. The aqueous layer was extracted once with ether. The combined organic layers were washed twice with water, made slightly acidic with dilute hydrochloric acid, and washed twice with saturated sodium chloride solution. Product 12f was
isolated after drying with anhydrous MgSO₄, solvent removal and column purification (Hexane/EAc = 1/5).

Sticky oil, 70%.

¹H NMR (400 MHz, CDCl₃): δ 0.73 (t, J = 7.2 Hz, 3H), 1.71-1.78 (m, 1H), 1.92-1.98 (m, 1H), 4.54 (d, J = 10.8 Hz, 1H), 4.59 (d, J = 10.8 Hz, 1H), 7.23-7.37 (m, 5H).

¹³C NMR (100 MHz, CDCl₃): δ 8.24, 21.86, 32.31, 42.66, 86.19, 126.17, 126.94, 128.60, 142.02.

IR (neat): 2973, 1549, 1375, 700 cm⁻¹.

HRMS (ESI): m/z calcd. for C₁₁H₁₅NNaO₂ (M + Na)⁺ 216.0995; found: 216.0993.

To a solution of S-5 (5 mmol) in THF/MeOH = 10/1 (20 mL) at 0 °C under argon, was added NaBH₄ (0.38 g, 10 mmol) slowly. After stirring for 20 min, the reaction was treated with 1N HCl and extracted with Et₂O three times. The combined organic layers were washed with brine (30 mL), dried (MgSO₄), filtered and evaporated to leave the crude product, which was purified by column chromatography over silica gel (hexane:ethyl acetate = 9:1) to provide 12g (1.42 g, 91%) as a sticky oil.

¹H NMR (400 MHz, CDCl₃): δ 1.37 (d, J = 6.8 Hz, 3H), 3.59-3.65 (m, 1H), 4.47 (dd, J = 8.4, 12 Hz, 1H), 4.54 (dd, J = 7.6, 12 Hz, 1H), 7.20-7.35 (m, 5H).

¹³C NMR (100 MHz, CDCl₃): δ 18.71, 38.63, 81.85, 126.89, 127.56, 128.96, 140.86.

IR (neat): 2973, 1552, 1383, 1022, 766, 701 cm⁻¹.
Scheme S-6. Preparation of nitroalkane 12h/12i.

**Step 1:** Based on a reported method,[4] (S)-cat. (20 mol%) was added to a solution of (E)-3-phenylbut-2-enal (584 mg, 4 mmol) in nitromethane (6.9 g, 28 equiv.) at room temperature. After stirring the reaction mixture at room temperature for 3 days, nitromethane was removed under reduced pressure. The residue was purified by silica gel flash column chromatography (using CH_2Cl_2/Hexane (1/1) and then AcOEt:hexane = 1:2) to afford compound S-6 (50%).

**Synthesize 12h:** To a solution of aldehyde S-6 (2 mmol) in THF (10 ml) and MeOH (1 ml) was added NaBH_4 (3 mmol) slowly at 0 °C. The reaction mixture was slowly warmed to r.t. and stirred for 30 min. After this time, the reaction mixture was quenched by adding sat. NH_4Cl solution (very slowly, being careful of evolving gas) and extracted with Ethyl Acetate. The combined organic phase was dried over anhydrous MgSO_4, concentrated in vacuum, filtered, and the crude alcohol purified by silica gel chromatography (Hexane/Ethyl Acetate = 1/1) to give 12h (> 95%).

**1H NMR** (400 MHz, CDCl_3): δ 1.57 (s, 3H), 1.96-2.03 (m, 1H), 2.13-2.20 (m, 1H), 3.42-3.48 (m, 1H), 3.54-3.60 (m, 1H), 4.65 (s, 2H), 7.23-7.37 (m, 5H).
^{13}C\text{NMR} (100 MHz, CDCl\textsubscript{3}): \delta 22.94, 41.34, 42.00, 58.94, 85.96, 125.86, 127.28, 128.81, 141.87.

IR (neat): 3392, 1548, 1446, 1053, 1032, 766, 702, 647 cm\textsuperscript{-1}.

HRMS (ESI): \textit{m/z} calcd. for C\textsubscript{11}H\textsubscript{15}NNaO\textsubscript{3} (M + Na)\textsuperscript{+} 232.0944; found: 232.0947.

**Synthesis of 12i:** To a solution of aldehyde S-6 (2 mmol) in t-BuOH (10 ml), 2-methyl-2-butene (1 ml) and Na\textsubscript{2}HPO\textsubscript{4}\cdot2H\textsubscript{2}O (4 mmol) were added, before adding NaClO\textsubscript{2} (6 mmol in 5 mL H\textsubscript{2}O) slowly at 0 °C. The mixture was stirred for 1.5 h and the reaction was quenched by the addition of saturated aqueous NaHCO\textsubscript{3}, and the water phase was washed with AcOEt. Following adjustment of pH to pH = 2 with 2M aqueous HCl, the aqueous phase was saturated with NaCl and extracted with AcOEt three times. The collected organic phase was dried over anhydrous MgSO\textsubscript{4} concentrated in vacuum, and the crude carboxylic acid S-7 was directly used for esterification without purification.

Under Ar, the carboxylic acid S-7 (about 2 mmol) was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (10 mL) and MeOH (0.5 mL) was added. The reaction mixture was cooled to 0°C and EDC•HCl (2 mmol) was added, followed by DMAP (0.4 mmol). The reaction was quenched with \textit{sat.} NH\textsubscript{4}Cl solution after 12h, extracted with CH\textsubscript{2}Cl\textsubscript{2} and the combined organic phases were dried over anhydrous MgSO\textsubscript{4}, filtered and evaporated to afford the crude product, which was purified by silica gel chromatography (Hex/EA = 5/1).

\[
\begin{array}{c}
\text{MeOOC} \\
\text{\begin{tikzpicture}
\draw (0,0) -- (0.5,0.5) -- (1,0);
\end{tikzpicture}}
\end{array}
\]

\textit{Sticky oil.}

^{1}H\text{NMR} (400 MHz, CDCl\textsubscript{3}): \delta 1.624 (s, 3H), 2.90 (d, J = 15.6Hz, 1H), 2.97 (d, J = 16 Hz, 1H), 3.59 (s, 3H), 4.87 (d, J = 11.6 Hz, 1H), 4.91 (d, J = 11.6 Hz, 1H), 7.24-7.37 (m, 5H).
$^{13}\text{C NMR}$ (100 MHz, CDCl$_3$): $\delta$ 24.01, 40.71, 42.81, 51.64, 83.71, 125.43, 127.45, 128.78, 141.84, 170.96.

IR (neat): 2953, 1737, 1550, 1446, 1374, 1210, 1176, 766, 699 cm$^{-1}$.

HRMS (ESI): $m/z$ calcd. for C$_{12}$H$_{15}$NNaO$_4$ (M + Na)$^+$ 260.0893; found: 260.0903.

Scheme S-7. Preparation of nitroalkane 12j.

**Synthesis of 12j**: Compound 12h (0.5 mmol) was dissolved in CHCl$_3$ (5 mL) and CH$_2$(OMe)$_2$ (15 equiv.) was added. P$_2$O$_5$ was added slowly until 12i disappeared as monitored by TLC (Hexane/Ethyl Acetate = 5/1). After this time, the reaction was diluted with CHCl$_3$, filtered through a short silica gel column and washed with CHCl$_3$, and the collected organics were evaporated under vacuum to afford the pure product 12j quantitatively.

$^1\text{H NMR}$ (400 MHz, CDCl$_3$): $\delta$ 1.58 (s, 3H), 2.03-2.10 (m, 1H), 2.16-2.23 (m, 1H), 3.27 (s, 3H), 2.28-3.34 (m, 1H), 3.38-3.37 (m, 1H), 3.41-3.37 (m, 1H), 4.47 (d, $J = 5.6$ Hz, 1H), 4.49 (d, $J = 5.6$ Hz, 1H), 4.61 (d, $J = 11.2$ Hz, 1H), 4.65 (d, $J = 11.2$ Hz, 1H), 7.23-7.36 (m, 5H).

$^{13}\text{C NMR}$ (100 MHz, CDCl$_3$): $\delta$ 22.79, 39.40, 41.37, 55.23, 63.81, 86.03, 96.38, 125.89, 127.22, 128.74, 141.82.

IR (neat): 1548, 768, 716, 698 cm$^{-1}$.

HRMS (ESI): $m/z$ calcd. for C$_{13}$H$_{19}$NNaO$_4$ (M + Na)$^+$ 276.1206; found: 276.1216.
3. Kinetic study of α,α-diiodonitroalkane 2a with MeOH.

3.1 $^1$H NMR analysis.

![Chemical structure and NMR spectra](image)

Figure S-1. Comparisim by $^1$H NMR showing reaction characters: a) with NIS (20 mol%); b) with 20 mol% KI (20 mol%).

**Procedure:** To a 10 mL reaction tube, α,α-diiodonitroalkane 4-2a (0.4 mmol) and dry CH$_3$CN (4 mL, pre-saturated with O$_2$) were mixed and put under an O$_2$-balloon atmosphere. After
CH\textsubscript{2}Br\textsubscript{2} (0.4 mmol) was added as internal standard, MeOH (2.0 mmol) and K\textsubscript{2}CO\textsubscript{3} (0.6 mmol) were added at r.t. under fast, but smooth stirring. Every 10 minutes, 100 μL of reaction mixture was removed and diluted with CDCl\textsubscript{3} (600 μL) for \textsuperscript{1}H NMR analysis, wherein the yield of ester was assayed by \textsuperscript{1}H NMR integration based on the internal standard (CH\textsubscript{2}Br\textsubscript{2}). See next page for sample spectra.

3.2 React IR analysis

Procedure: To a reaction flask (10 mL), α,α-diiodonitroalkane \textbf{2a} (0.3 mmol), K\textsubscript{2}CO\textsubscript{3} (0.15 mmol) and dry CH\textsubscript{3}CN (6 mL, pre-saturated with O\textsubscript{2}) were mixed and put under an O\textsubscript{2}-balloon atmosphere. The react IR probe was inserted into the solution. After all yellow solid dissolved in CH\textsubscript{3}CN, MeOH (1.5 mmol, 5.0 equiv.) was added at r.t. under fast, but smooth stirring. Finally, I\textsubscript{2} or NEt\textsubscript{4}I was added in one portion and IR spectra were recorded every minute. After the reaction finished, CHCl\textsubscript{3} was added and the precipitate formed was filtered, collected and washed with CHCl\textsubscript{3}, dissolved in D\textsubscript{2}O and then checked by NMR directly. The collated organic solution was washed with \textit{sat.} Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, dried over anhydrous magnesium sulfate, and then evaporated \textit{in vacuo} to give the ester \textbf{6} without further purification.

\begin{center}
Product in organic phase:
\end{center}

\begin{center}
\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 2.62 (t, \textit{J} = 8.0 Hz, 2H), 2.94 (t, \textit{J} = 8.0 Hz, 2H), 7.18-7.30 (m, 5H).
\end{center}

\begin{center}
\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 30.92, 35.68, 51.60, 126.25, 128.25, 128.49, 140.49, 173.33.
\end{center}

\begin{center}
HRMS (ESI): \textit{m/z} calcd. for C\textsubscript{10}H\textsubscript{12}NaO\textsubscript{2} [M+Na]\textsuperscript{+} 187.0730; found:187.0716.
\end{center}
Product in water phase:

(The data is consistent with PHCH$_2$CH$_2$COOH mixed with KOH in D$_2$O)

$^1$H NMR (400 MHz, D$_2$O): δ 2.66-2.70 (m, 2H), 2.93-2.97 (m, 2H), 7.18-7.30 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 27.98, 32.86, 123.79, 125.66, 125.97, 137.54, 175.80.

IR band: 1560 cm$^{-1}$

IR band: 1739 cm$^{-1}$
Figure S-2. React IR study of \(\alpha,\alpha\)-diiodonitroalkane \(2a\) reacting with MeOH with different additives.

4. Kinetic study of \(\alpha,\alpha\)-diiodonitroalkane \(2a\) with \(\text{CF}_3\text{CH}_2\text{NH}_2\).

Procedure: To a 10 mL reaction tube, \(\alpha,\alpha\)-diiodonitroalkane \(2a\) (0.4 mmol) and dry \(\text{CH}_3\text{CN}\) (4 mL, pre-saturated with \(\text{O}_2\)) were mixed and put under an \(\text{O}_2\)-balloon atmosphere. \(\text{CH}_2\text{Br}_2\) (0.4 mmol) was added as internal standard. After this preparation, \(\text{CF}_3\text{CH}_2\text{NH}_2\) (0.6 mmol) and \(\text{K}_2\text{CO}_3\) (0.6 mmol) were added at r.t. under fast, but smooth stirring. Every 10 minutes, 100 \(\mu\text{L}\) of reaction mixture was removed, diluted with \(\text{CDCl}_3\) (600 \(\mu\text{L}\)), and the yield of the amide product \(5a\) assayed by \(^1\text{H}\) NMR integration based on the internal standard (\(\text{CH}_3\text{Br}_2\)).
Figure S-3. $^1$H NMR study of $\alpha,\alpha$-diidonitroalkane 2a reacting with CF$_3$CH$_2$NH$_2$.

White solid, yield = 50%.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.53 (t, $J = 7.6$ Hz, 2H), 2.97 (t, $J = 7.6$ Hz, 2H), 3.82-3.90 (m, 2H), 5.63 (br s, 1H), 7.16-7.30 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 31.33, 38.11, 40.55 (q, $J = 35$ Hz, 1C), 123.95 (q, $J = 276.8$ Hz, 1C), 126.42, 128.25, 128.61, 140.27.

IR (neat): 3308, 2360, 1662, 1558, 1158, 701 cm$^{-1}$.

HRMS (ESI): $m/z$ calcd. for C$_{11}$H$_{12}$F$_3$NNaO (M + Na)$^+$ 254.0763; found 254.0765.

5. $^1$H NMR study of benzylamine with $\alpha,\alpha$-diiodnitroalkane 2a.

5.1 $^1$H NMR investigation of the reaction of $\alpha,\alpha$-diiodnitroalkane 2a and benzylamine
Immediately after $\alpha,\alpha$-diiodonitroalkane 2a was mixed with benzylamine (1.5 equiv) in CD$_3$CN at r.t., the reaction was monitored by $^1$H NMR spectroscopy within 5 min. We observed the monoiodonitroalkane being generated (cf. Figure S-4, blue and purple spectrums). After work-up with water, we observed benzylaldehyde. We thus propose a side reaction as given in Scheme S-8. However, when CF$_3$CH$_2$NH$_2$ was used instead of benzylamine, this side reaction was not observed (cf. red and purple spectrums).
5.2 Kinetic study of benzylamine with \(\alpha,\alpha\)-diiodonitroalkane 2a using \(^1\text{H}\) NMR.

**Figure S-5.** \(^1\text{H}\) NMR study of benzylamine with \(\alpha,\alpha\)-diiodonitroalkane 2a

**Procedure:** To a 10 mL reaction tube, \(\alpha,\alpha\)-diiodonitroalkane 2a (0.4 mmol), dry CH\(_3\)CN (4 mL, pre-saturated with O\(_2\)) were mixed and put under an O\(_2\)-balloon atmosphere. CH\(_2\)Br\(_2\) (0.4 mmol) was added as an internal standard. After this preparation, PhCH\(_2\)NH\(_2\) (2.0 mmol) and K\(_2\)CO\(_3\) (0.6 mmol) were added under fast, but smooth stirring at -10 °C. Every 10 minutes, 100 μL of reaction mixture was removed, diluted by CDCl\(_3\) (600 μL), and analysed by \(^1\text{H}\) NMR spectroscopy.
Figure S-6. Comparison of the effect of I at -10 °C during oxidative amide formation.

White solid, yield = 75%.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.48 (t, $J$ = 7.6 Hz, 2H), 2.96 (t, $J$ = 7.6 Hz, 2H), 3.45 (d, $J$ = 5.6 Hz, 2H), 5.95 (br s, 1H), 7.11-7.30 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 31.71, 38.38, 43.49, 126.23, 127.38, 127.68, 128.39, 128.53, 128.61, 138.19, 140.78, 172.02.

IR (neat): 3287, 1637, 1541, 1454, 697 cm$^{-1}$.

HRMS (ESI): $m/z$ calcd. for C$_{16}$H$_{17}$NNaO (M + Na)$^+$ 262.1202; found: 262.1203.
6. Effect of additives on induction time

<table>
<thead>
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<th>Additive (20 mol%)</th>
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<th>Induction time (min)</th>
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</thead>
<tbody>
<tr>
<td>none</td>
<td>25</td>
<td>50–60</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8–10</td>
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<tr>
<td>tBuOOH</td>
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<td>&lt; 5</td>
</tr>
<tr>
<td>AIBN</td>
<td>25</td>
<td>50–60</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8–10</td>
</tr>
<tr>
<td>BPO</td>
<td>25</td>
<td>50–60</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>13–15</td>
</tr>
<tr>
<td>TEMPO</td>
<td>25</td>
<td>30–40</td>
</tr>
</tbody>
</table>

AIBN: 2,2'-azobis(2-methylpropionitrile); BPO: benzoyl peroxide; TEMPO: 2,2,6,6-tetramethylpiperidinyloxy

**Typical procedure for above study:** A sequence of 10 mL reaction flasks was charged with α,α-diiodonitroalkane 2a (0.3 mmol; all from the same, freshly-made batch), K₂CO₃ (0.15 mmol), dry CH₃CN (6 mL, pre-saturated with O₂) and an O₂-balloon atmosphere. After all yellow 2a dissolved, each flask was charged with MeOH (1.5 mmol, 5.0 equiv.) and then the selected additive (20 mol%, see above table) under fast, but smooth stirring at r.t. The reaction was monitored by TLC (Hexane/CH₂Cl₂ = 1/1) and by observing the color changes (Figure S-5).
Figure S-7. Color change of the reaction at 50 °C (oil bath) without any additive.

7. Optimization, formation and characterization of esters.

![Diagram](attachment:image.png)

Table S1. Optimization of Oxidative Esterification Process.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Solvent</th>
<th>Time [h]</th>
<th>Yield [%]</th>
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<tbody>
<tr>
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<td>K(_2)CO(_3)</td>
<td>CH(_3)CN</td>
<td>24h</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>K(_2)CO(_3)</td>
<td>THF</td>
<td>24 h</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>K(_2)CO(_3)</td>
<td>CH(_2)Cl(_2)</td>
<td>24 h</td>
<td>trace</td>
</tr>
<tr>
<td>4(^b)</td>
<td>K(_2)CO(_3)</td>
<td>MeOH</td>
<td>6 h</td>
<td>71</td>
</tr>
<tr>
<td>5(^b)</td>
<td>Li(_2)CO(_3)</td>
<td>MeOH</td>
<td>6 h</td>
<td>62</td>
</tr>
<tr>
<td>6(^b)</td>
<td>Na(_2)CO(_3)</td>
<td>MeOH</td>
<td>12h</td>
<td>49</td>
</tr>
<tr>
<td>7(^b)</td>
<td>Cs(_2)CO(_3)</td>
<td>MeOH</td>
<td>1h</td>
<td>22</td>
</tr>
<tr>
<td>8(^b)</td>
<td>NaOMe</td>
<td>MeOH</td>
<td>1h</td>
<td>41</td>
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<tr>
<td>9(^b)</td>
<td>KOMe</td>
<td>MeOH</td>
<td>1h</td>
<td>59</td>
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<tr>
<td>10(^b,c)</td>
<td>KOMe</td>
<td>MeOH</td>
<td>1h</td>
<td>71</td>
</tr>
</tbody>
</table>

[a] Reactions were conducted with nitroalkane 12a (0.2 mmol), MeOH (1.0 mmol), base (0.4 mmol) under O\(_2\) atmosphere in CH\(_3\)CN (2 mL); [b] MeOH (2 mL) was used as the solvent; [c] KOMe (3 equiv) was used.

For optimization, we selected the readily prepared N-protected 1,1-dimethyl-2-nitroethanamine 12a and methanol for optimization to form the sterically hindered methyl ester 13a (Table S1,
Eq. (3)). $K_2CO_3$ was first selected as a suitable base in solvents of $CH_3CN$, THF or $CH_2Cl_2$. These reactions were found to be very slow due to the low solubility of $K_2CO_3$ limiting the formation of $\alpha$-iodinated intermediates (entries 1–3). Carbonate bases in MeOH as the solvent improved the reaction times and yields (entries 4–7). KOMe was found to be a superior choice to NaOMe (cf. entries 8 and 9), especially when used in 3 equivalents (entry 10).

**Typical procedure:** To a 10 mL flask, the nitroalkane 12 (0.2 mmol) was dissolved in distilled dry MeOH or EtOH (2 mL, pre-saturated with $O_2$) and MeOK (3 equiv.) was added with stirring for 5 min. After all solid dissolved, I$_2$ (1.2 equiv.) was added under fast, but smooth stirring. After the nitroalkane 12 disappeared by TLC monitoring, the reaction was quenched with sat. Na$_2$S$_2$O$_3$ solution and extracted with CHCl$_3$. The combined organic solution was dried over anhydrous magnesium sulfate, the solvent was removed *in vacuo*, and the crude product was columned by silica gel chromatography to give the pure methyl ester (13–15).

```
     O
    /    |
   CbzHN
     |    |
     |    O
     |    Me
```

Sticky oil, yield = 70%.

**$^1H$ NMR** (400 MHz, CDCl$_3$): $\delta$ 1.53 (s, 6H), 3.70 s, (3H), 5.07 (s, 2H), 5.38 (br s, 1H), 7.28-7.35 (m, 5H).

**$^{13}C$ NMR** (100 MHz, CDCl$_3$): $\delta$ 25.14, 52.61, 56.47, 66.52, 128.04, 128.07, 128.48, 128.52, 136.39, 154.88, 175.04.

**IR (neat):** 3355, 1717, 1552, 1456, 1292, 1252, 1153, 1075, 699 cm$^{-1}$.

**HRMS $m/z$** calcd. for C$_{13}$H$_{17}$NNaO$_4$ (M + Na)$^+$ 274.1050; found: 274.1054.
Sticky oil, yield = 60%.

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 1.14-1.24 (m, 3H), 1.53 (s, 6H), 4.16 (m, 2H), 5.06 (s, 2H), 5.39 (br s, 1H), 7.24-7.34 (m, 5H).

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 14.03, 25.01, 56.42, 61.54, 66.45, 128.04, 128.07, 128.48, 136.42, 174.56.

\( \text{IR (neat):} \) 3416, 1640, 1539, 742 cm\(^{-1}\).

\( \text{HRMS } m/z \) calcd. for C\(_{14}\)H\(_{20}\)NO\(_4\) (M + H){+} 266.1387; found: 266.1392.

Sticky oil, yield = 65%.

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 1.24-1.33 (m, 1 H), 1.39-1.49 (m, 2H), 1.59-1.63 (m, 3H), 1.80-1.87 (m, 2H), 1.98-2.02 (m, 2H).

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 3.66 (br s, 3H), 4.95 (br s, 1H), 5.07 (s, 2H), 7.28-7.36 (5H).

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 21.20, 25.11, 32.60, 52.28, 59.11, 66.67, 128.05, 136.37, 155.19, 174.82.

\( \text{IR (neat):} \) 3353, 2945, 128.10, 128.48, 128.52, 1734, 1523, 1455, 1281, 1258, 1236, 1069, 740, 699 cm\(^{-1}\).

\( \text{HRMS } m/z \) calcd. for C\(_{16}\)H\(_{21}\)NNaO\(_4\) (M + Na){+} 314.1363; found: 314.1365.
Sticky oil, yield = 68%.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.74-1.87 (m, 6H), 2.18-2.21 (m, 2H), 2.48-2.57 (m, 1H), 3.47 (s, 3H), 3.73 (s, 3H), 4.76 (s, 2H), 7.16-7.31 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 28.42, 32.46, 33.95, 41.35, 43.13, 52.14, 56.46, 77.85, 92.88, 126.112, 126.74, 128.38, 146.72, 175.17.

IR (neat): 2949, 1738, 1450, 1243, 1144, 1028, 701 cm$^{-1}$.

HRMS $m/z$ calcd. for C$_{16}$H$_{22}$NaO$_4$ (M + Na)$^+$ 301.1410; found: 301.1410.

Sticky oil, yield = 60%.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.81 (t, $J$ = 7.2 Hz, 3H), 1.52 (s, 3H), 1.92-1.99 (m, 1H), 2.05-2.12 (m, 1H), 3.64 (s, 3H), 7.20-7.35 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 9.11, 22.20, 31.80, 50.65, 52.01, 125.99, 126.58, 128.31, 143.84, 176.80.

IR (neat): 2974, 1731, 1240, 1147, 699 cm$^{-1}$.

HRMS (ESI): $m/z$ calcd. for C$_{12}$H$_{16}$NaO$_2$ (M + Na)$^+$ 215.1043; 215.1044.

White solid, yield = 75%.
\(^1\text{H NMR (400 MHz, CDCl}_3\)): \(\delta 1.93\) (s, 3H), 3.73 (s, 3H), 7.20-7.32 (m, 5H).

\(^{13}\text{C NMR (100 MHz, CDCl}_3\)): \(\delta 27.09, 52.48, 56.55, 126.81, 127.99, 128.07, 144.38, 175.63.\)

IR (neat): 2992, 1732, 1496, 1447, 1240, 699 cm\(^{-1}\).

HRMS \(m/z\) calcd. for \(\text{C}_{16}\text{H}_{16}\text{NaO}_2\) (M + Na)\(^+\) 263.1043; found: 263.1042.

White solid, yield = 79%.

\(^1\text{H NMR (400 MHz, CDCl}_3\)): \(\delta 3.68\) (s, 3H), 3.71 (s, 2H), 6.65-6.67 (s, 2H), 5.38 (br s, 1H), 7.28-7.35 (m, 5H).

\(^{13}\text{C NMR (100 MHz, CDCl}_3\)): \(\delta 44.42, 52.18, 62.04, 126.23, 126.81, 127.44, 127.63, 129.25, 130.83, 137.28, 142.73, 173.99.\)

IR (neat): 3029, 1732, 1497, 1446, 1219, 700 cm\(^{-1}\).

HRMS \(m/z\) calcd. for \(\text{C}_{22}\text{H}_{20}\text{NaO}_2\) (M + Na)+ 339.1356; found: 339.1355.

Yield = 72%, sticky oil.

\(^1\text{H NMR (400 MHz, CDCl}_3\)): \(\delta 1.68\) (s, 3H), 2.80 (d, \(J = 16.4\) Hz, 1H), 3.26 (d, \(J = 16.4\) Hz, 1H), 3.63 (s, 3H), 3.86 (s, 3H), 7.22-7.34 (m, 5H). \(^{13}\text{C NMR (100 MHz, CDCl}_3\)): \(\delta 23.35, 43.42, 48.23, 51.61, 52.39, 125.55, 127.18, 128.61, 142.54, 171.49, 175.29.\)

IR (neat): 3446, 1647, 715 cm\(^{-1}\).

HRMS (ESI): \(m/z\) calcd. for \(\text{C}_{13}\text{H}_{16}\text{NaO}_4\) (M + Na)+ 259.0941; found: 259.0944.
Yield = 70%, sticky oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.58 (s, 3H), 2.18-2.25 (m, 1), 2.39-2.46 (m, 1H), 3.30 (s, 3H), 3.48 (t, J = 7.2 Hz, 2H), 3.64 (s, 3H), 4.53 (s, 2H), 7.20-7.33 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 23.11, 38.47, 48.76, 52.15, 55.20, 64.40, 96.37, 125.78, 126.84, 128.47, 143.34, 176.35.

IR (neat): 3454, 1637, 697 cm$^{-1}$.

HRMS (ESI): $m/z$ calcd. for C$_{14}$H$_{20}$NaO$_4$ (M + Na)$^+$ 275.1254; found: 275.1259.

Yield = 80%, sticky oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.60 (s, 3H), 2.35-2.43 (m, 1H), 2.63-2.69 (m, 1H), 4.09-4.15 (m, 1H), 4.28-4.33 (m, 1H), 7.25-7.40 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 25.45, 38.05, 47.49, 65.00, 125.84, 127.39, 128.83, 141.01, 180.02.

IR (neat): 2982, 1761, 1496, 1446, 1368, 1201, 1174, 768, 700 cm$^{-1}$.

HRMS (ESI): $m/z$ calcd. for C$_{11}$H$_{12}$NaO$_2$ (M + Na)$^+$ 199.0730; found: 199.0732.

K$_2$CO$_3$ used instead of KOMe. Sticky oil, yield = 60%.

The NMR data is consistent with previous report$^5$. 
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.65 (dd, $J = 5.2, 18.8$ Hz, 1H), 3.19 (dd, $J = 10, 16.8$ Hz, 1H), 3.65 (s, 3H), 3.66 (s, 3H), 4.07 (dd, $J = 5.2, 10$ Hz, 1H), 7.23-7.33 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 37.60, 47.06, 51.85, 52.35, 127.66, 127.70, 128.87, 137.63, 171.96, 173.41.

Sticky oil, yield = 61%

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.49 (d, $J = 7.2$ Hz, 3H), 3.65 (s, 3H), 3.71 (q, $J = 7.2$ Hz, 1H), 7.22-7.33 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 18.57, 45.39, 51.99, 127.11, 127.44, 128.61, 140.53, 174.99.

IR (neat): 2982, 1736, 1580, 1454, 1209, 1166, 699 cm$^{-1}$.

HRMS (ESI): $m/z$ calcd. for C$_{10}$H$_{12}$NaO$_2$ (M+Na)$^+$ 187.0730; Found 187.0727.

HRMS (ESI): $m/z$ calcd. for C$_{12}$H$_{14}$NaO$_4$ (M + Na)$^+$ 245.0784; found: 245.0788.

8. X-Ray structure of $\alpha,\alpha$-diiodonitroalkane 2a

The single crystal of 2a suitable for X-ray analysis was grown in a solution of dichloromethane/hexane at -30 °C under Ar. A yellow block crystal of C$_9$H$_9$I$_2$NO$_2$ having approximate dimensions of 0.400×0.400×0.300 mm was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB mini diffractometer using graphite monochromated Mo-Ka radiation. The crystal-to-detector distance was 50.11 mm. The data were collected at a temperature of -123±1 °C to a maximum 2q value of 55.0o. A total of 540 oscillation images were collected. A sweep of data was done using w scans from -60.0 to 120.0o in 1.00o step, at c = 54.0o and f = 0.0o. The exposure rate was 12.0 [sec./o]. The detector swing angle was 30.00o. A second sweep was performed using w scans from -60.0 to 120.0o in 1.00o
step, at c = 54.0° and f = 120.0°. The exposure rate was 12.0 [sec./o]. The detector swing angle was 30.00°. Another sweep was performed using w scans from −60.0 to 120.0° in 1.00° step, at c = 54.0° and f = 240.0°. The exposure rate was 12.0 [sec./o]. The detector swing angle was 30.00°. Another sweep was performed using w scans from −60.0 to 120.0° in 1.00° step, at c=54.0° and f = 0.0°. The exposure rate was 12.0 [sec./o]. The detector swing angle was 30.20°. Another sweep was performed using w scans from −60.0 to 120.0° in 1.00° step, at c = 54.0° and f = 120.0°. The exposure rate was 12.0 [sec./o]. The detector swing angle was 30.20°. Another sweep was performed using w scans from −60.0 to 120.0° in 1.00° step, at c = 54.0° and f = 240.0°. The exposure rate was 12.0 [sec./o]. The detector swing angle was 30.20°. The crystal-to-detector distance was 50.11 mm. Readout was performed in the 0.073 mm pixel mode. Crystallographic data has been deposited with the Cambridge Crystallographic Data Center, CCDC reference number: 1437079.

A. Crystal Data

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### Lattice Parameters

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### Space Group

- **Pbca (#61)**

### Z value

- 8

### Dcalc

- 2.421 g/cm³

### F000

- 1536.00

### m(MoKa)

- 54.758 cm⁻¹

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#### B. Intensity Measurements

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<td><strong>Data Images</strong></td>
<td>540 exposures</td>
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<td><strong>Detector Swing Angle</strong></td>
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Exposure Rate: 12.0 sec./°

Detector Swing Angle: 30.0°

ω oscillation Range (χ=54.0, φ=240.0): -60.0 - 120.0°

Detector Swing Angle: 30.0°

ω oscillation Range (χ=54.0, φ=0.0): -60.0 - 120.0°

Detector Swing Angle: 30.2°

ω oscillation Range (χ=54.0, φ=120.0): -60.0 - 120.0°

Detector Swing Angle: 30.2°

ω oscillation Range (χ=54.0, φ=240.0): -60.0 - 120.0°

Detector Swing Angle: 30.2°

Detector Position: 50.11 mm

Pixel Size: 0.073 mm

2θmax: 55.0°

No. of Reflections Measured
- Total: 20398
- Unique: 2620 (Rint = 0.0807)

Corrections
- Lorentz-polarization
- Absorption
  (trans. factors: 0.103 - 0.193)
C. Structure Solution and Refinement

Structure Solution

Charge Flipping (Superflip)

Refinement

Full-matrix least-squares on F^2

Function Minimized

\[ \sum w (F_o^2 - F_c^2)^2 \]

Least Squares Weights

\[ \omega = \frac{1}{s^2(F_o^2) + (0.0820 \cdot P)^2 + 55.3747 \cdot P} \]

where \( P = (\text{Max}(F_o^2,0) + 2F_c^2)/3 \)

\( 2\theta_{\text{max}} \) cutoff

55.0\(^0\)

Anomalous Dispersion

All non-hydrogen atoms

No. Observations (All reflections)

2620

No. Variables

127

Reflection/Parameter Ratio

20.63

Residuals: R1 (I>2.00s(I))

0.0716

Residuals: R (All reflections)

0.0743

Residuals: \( \omega R^2 \) (All reflections)

0.2096

Goodness of Fit Indicator

1.193

Max Shift/Error in Final Cycle

0.001

Maximum peak in Final Diff. Map

3.43 e/Å\(^3\)

Minimum peak in Final Diff. Map

-2.81 e/Å\(^3\)
**Table 1.** Atomic coordinates and B_{iso}/B_{eq}  

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<th>atom</th>
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<th>y</th>
<th>z</th>
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<td>0.13541(5)</td>
<td>2.46(2)</td>
</tr>
<tr>
<td>I2</td>
<td>0.17729(8)</td>
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<td>0.26361(6)</td>
<td>3.22(2)</td>
</tr>
<tr>
<td>O7</td>
<td>-0.0352(10)</td>
<td>0.9763(10)</td>
<td>0.3179(6)</td>
<td>4.1(2)</td>
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<tr>
<td>O8</td>
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<td>0.8909(10)</td>
<td>0.2095(8)</td>
<td>4.4(2)</td>
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<tr>
<td>N3</td>
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<td>0.9582(9)</td>
<td>0.2457(7)</td>
<td>2.62(18)</td>
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<tr>
<td>C6</td>
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<td>1.0264(10)</td>
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<tr>
<td>C12</td>
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<td>0.7723(10)</td>
<td>0.0811(7)</td>
<td>2.20(19)</td>
</tr>
<tr>
<td>C13</td>
<td>0.0936(10)</td>
<td>0.9522(10)</td>
<td>0.1211(7)</td>
<td>2.19(18)</td>
</tr>
<tr>
<td>C14</td>
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<td>0.0630(11)</td>
<td>3.4(3)</td>
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<tr>
<td>C15</td>
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<td>0.6131(12)</td>
<td>-0.0079(11)</td>
<td>3.7(3)</td>
</tr>
<tr>
<td>C16</td>
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<td>0.6333(13)</td>
<td>-0.0530(9)</td>
<td>4.0(3)</td>
</tr>
<tr>
<td>C17</td>
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<td>0.7200(13)</td>
<td>-0.0327(9)</td>
<td>3.3(2)</td>
</tr>
<tr>
<td>C18</td>
<td>0.2842(11)</td>
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<td>2.6(2)</td>
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<tr>
<td>C19</td>
<td>0.1619(14)</td>
<td>0.8498(13)</td>
<td>0.1520(8)</td>
<td>3.5(3)</td>
</tr>
</tbody>
</table>

\[
B_{eq} = \frac{8}{3} p^2 (U_{11}(aa*)^2 + U_{22}(bb*)^2 + U_{33}(cc*)^2 + 2U_{12}(aa*bb*)\cos \gamma + 2U_{13}(aa*cc*)\cos \beta + 2U_{23}(bb*cc*)\cos \alpha) 
\]

**Table 2.** Atomic coordinates and B_{iso} involving hydrogen atoms  

<table>
<thead>
<tr>
<th>atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B_{iso}</th>
</tr>
</thead>
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<td>0.14067</td>
<td>0.99951</td>
<td>0.08454</td>
<td>2.628</td>
</tr>
<tr>
<td>H13B</td>
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<td>0.08760</td>
<td>2.628</td>
</tr>
<tr>
<td>Atom</td>
<td>U11</td>
<td>U22</td>
<td>U33</td>
<td>U12</td>
</tr>
<tr>
<td>-------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>H14</td>
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<td>0.66772</td>
<td>0.09711</td>
<td>4.065</td>
</tr>
<tr>
<td>H15</td>
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<td>0.55365</td>
<td>-0.02311</td>
<td>4.485</td>
</tr>
<tr>
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<td>0.25146</td>
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<tr>
<td>H17</td>
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</tr>
<tr>
<td>H18</td>
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<td>0.04843</td>
<td>3.095</td>
</tr>
<tr>
<td>H19A</td>
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<td>0.87762</td>
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<td>4.186</td>
</tr>
<tr>
<td>H19B</td>
<td>0.11848</td>
<td>0.80646</td>
<td>0.19336</td>
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</table>

**Table 3.** Anisotropic displacement parameters

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<th>Atom</th>
<th>U11</th>
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<th>U33</th>
<th>U12</th>
<th>U13</th>
<th>U23</th>
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<tr>
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<td>0.0280(4)</td>
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<td>0.0096(3)</td>
<td>-0.0029(3)</td>
<td>0.0017(3)</td>
</tr>
<tr>
<td>I2</td>
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<td>0.0399(5)</td>
<td>0.0425(6)</td>
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<td>-0.0068(4)</td>
<td>0.0006(4)</td>
</tr>
<tr>
<td>O7</td>
<td>0.062(7)</td>
<td>0.057(7)</td>
<td>0.036(5)</td>
<td>-0.013(6)</td>
<td>0.008(5)</td>
<td>-0.004(5)</td>
</tr>
<tr>
<td>O8</td>
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<td>0.053(7)</td>
<td>0.070(7)</td>
<td>-0.019(5)</td>
<td>0.007(6)</td>
<td>-0.017(6)</td>
</tr>
<tr>
<td>N3</td>
<td>0.040(6)</td>
<td>0.027(5)</td>
<td>0.032(5)</td>
<td>0.008(5)</td>
<td>0.001(4)</td>
<td>0.000(4)</td>
</tr>
<tr>
<td>C6</td>
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<td>0.027(6)</td>
<td>0.032(6)</td>
<td>0.012(5)</td>
<td>-0.007(5)</td>
<td>0.001(5)</td>
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<tr>
<td>C12</td>
<td>0.027(5)</td>
<td>0.032(6)</td>
<td>0.025(5)</td>
<td>0.018(4)</td>
<td>0.002(4)</td>
<td>0.001(4)</td>
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<tr>
<td>C13</td>
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<td>0.028(6)</td>
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<td>0.000(4)</td>
<td>0.001(4)</td>
</tr>
<tr>
<td>C14</td>
<td>0.031(6)</td>
<td>0.026(6)</td>
<td>0.072(10)</td>
<td>0.009(5)</td>
<td>0.003(6)</td>
<td>0.015(6)</td>
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<tr>
<td>C15</td>
<td>0.054(9)</td>
<td>0.025(6)</td>
<td>0.063(9)</td>
<td>0.005(6)</td>
<td>-0.012(8)</td>
<td>-0.007(6)</td>
</tr>
<tr>
<td>C16</td>
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<td>0.039(7)</td>
<td>0.042(8)</td>
<td>0.019(8)</td>
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<td>-0.013(6)</td>
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<tr>
<td>C17</td>
<td>0.040(7)</td>
<td>0.042(8)</td>
<td>0.044(7)</td>
<td>0.013(6)</td>
<td>0.012(6)</td>
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<tr>
<td>C18</td>
<td>0.035(6)</td>
<td>0.020(5)</td>
<td>0.042(7)</td>
<td>-0.001(5)</td>
<td>0.005(5)</td>
<td>-0.002(5)</td>
</tr>
</tbody>
</table>
The general temperature factor expression: \( \exp(-2p^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl}) \)

### Table 4. Bond lengths (Å)

<table>
<thead>
<tr>
<th>atom</th>
<th>atom</th>
<th>distance</th>
<th>atom</th>
<th>atom</th>
<th>distance</th>
</tr>
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<tbody>
<tr>
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<td>C6</td>
<td>2.145(12)</td>
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<td>1.37(2)</td>
<td>C17</td>
<td>C18</td>
<td>1.389(19)</td>
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</tbody>
</table>
9. References


10. $^1$H, $^{13}$C NMR and HPLC Spectra (see separate SI file)