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

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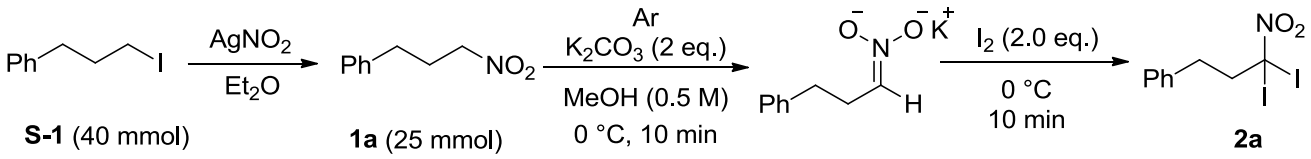
1. General Information

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_3CN), 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).

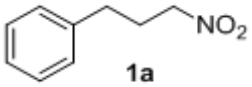
React IR Information: React IR 15, Probe A: ReactIR 15 (SN: unspecified) with MCT Detector using HappGenzel apodization; DiComp (Diamond) probe (SN: unspecified) connected via AgX 6mm 1.5m Fiber (Silver Halide); Sampling 2500 to 650 at 8 wavenumber resolution; Scan option: AutoSelect; Gain: 1.

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 Et_2O (50 mL) and $AgNO_2$ 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 **v**ia silica gel chromatography (Hex/EA = 10/1) to give pure **1a** (62.5%) as a colorless sticky oil.



^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28-2.35 (m, 2H), 2.71 (t, *J* = 7.2 Hz, 2H), 4.35 (t, J = 7.2 Hz, 2H), 7.16-7.32 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 28.82, 32.21, 74.64, 126.58, 128.42, 128.70, 139.44.

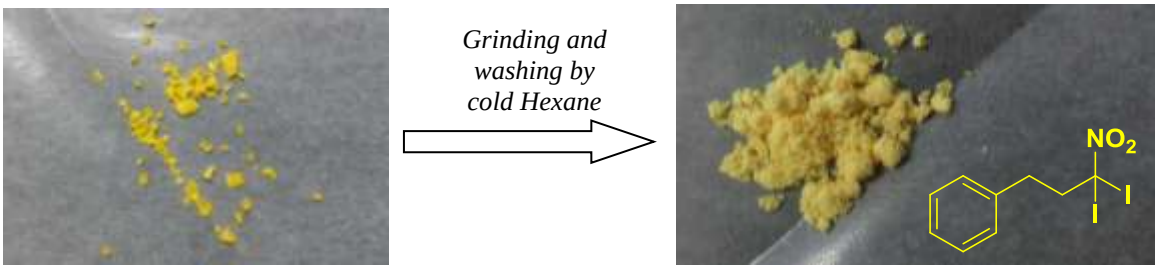
IR (neat): 2929, 1552, 1383, 701 cm^{-1}.

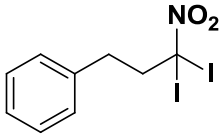
HRMS (ESI): *m/z* calcd. for $C_9H_{11}NNaO_2$ $(M + Na)^+$ 188.0682; found: 188.0885.

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, K_2CO_3 (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 I_2 (2.0 eq.) was added at the same reaction temperature. After stirring for 10 min, the mixture was quenched with

NH_4Cl (400 mL) and extracted with pre-cooled CH_2Cl_2 (-30 ºC, 150 × 2mL). The organic phase was dried over $MgSO_4$ at -30 ºC, 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 (CH_2Cl_2 + hexane) at -30 ºC 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.

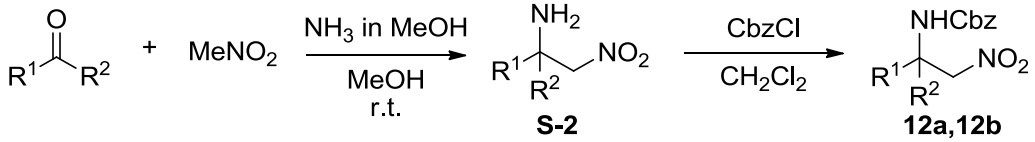
Caution: Employing highly pure α,α-diiodonitroalkane **2a** is key to obtaining accurate kinetic profiles for oxidative reactions. If the crystals are purple-red, the induction times become very short, presumably due to iodine-based impurities.





^{1}H NMR (400 MHz, CD_3CN): δ 2.76-2.80 (m, 2H), 3.01-3.14 (m, 2H), 7.23-7.36 (5H).

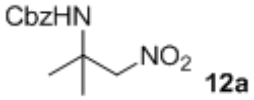
^{13}C NMR (100 MHz, CD_3CN): δ 23.29, 42.10, 59.39, 131.91, 133.97, 143.68.



Scheme S-2. Preparation of nitroalkane **12a/12b**.

Synthesis of S-2: To a 100 mL flask containing the ketone (40 mmol) and $MeNO_2$ (200 mmol) was added a saturated methanolic solution of NH_3 (20 mL) and the reaction was stirred at r.t. under an NH_3 atmosphere (NH_3 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 CH_2Cl_2 (50 mL) and cooled to 0 °C, CbzCl (20 mmol) and NEt_3 (20 mmol) were added. After stirring at r.t. for 3 h, the reaction mixture was quenched with *sat.* $NaHCO_3$ solution and extracted with $CHCl_3$. The combined organic solution was dried over anhydrous magnesium sulfate, the solvent was removed *in vacuo* and the give crude product was columned by silica gel chromatography (Hexane/ Ethyl Acetate = 3/1) to give pure **12a** or **12b**.



12a

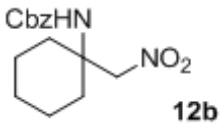
White solid, yield = 80% (over 2 steps)

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (s, 6H), 4.73 (s, 2H), 4.89 (br s, 1H), 5.09 (s, 2H), 7.30-7.35 (s, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{12}H_{16}N_2NaO_4$ $(M + Na)^+$ 275.1002; found: 275.1400.



12b

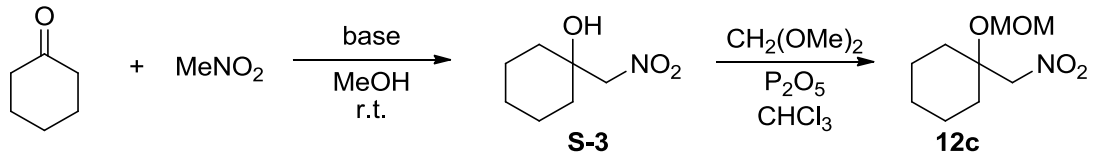
Sticky oil, yield = 70% (over steps)

^{1}H NMR (400 MHz, $CDCl_3$): δ 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ 20.95, 25.07, 32.90, 54.62, 66.60, 80.21, 127.91, 128.17, 128.56, 136.20, 154.64.0, 154.64.

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

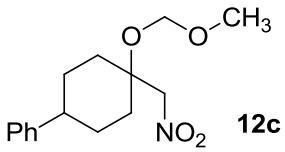
HRMS (ESI): *m/z* calcd. for $C_{15}H_{20}N_2NaO_4$ $(M + Na)^+$ 315.1315; found: 315.1318.



Scheme S-3. Preparation of α,α-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_2O_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.



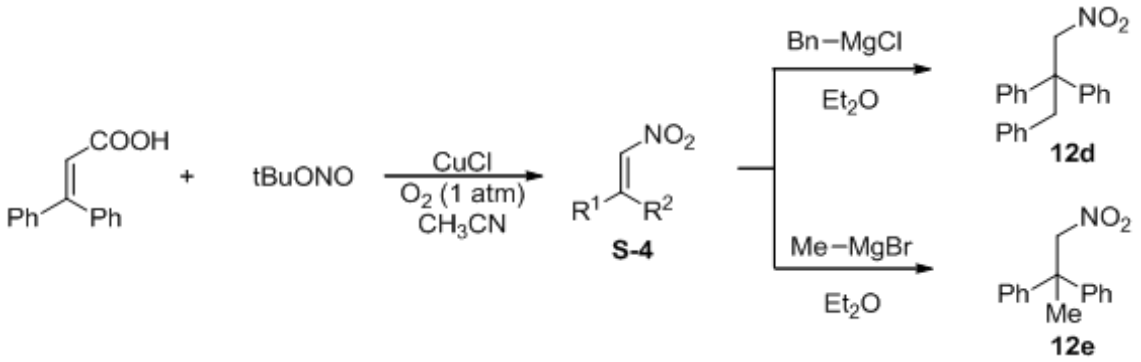
12c

^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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.

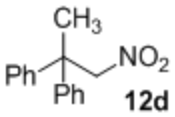


Scheme S-4. Preparation of nitroalkane **12d**/**12e**.

Step 1:[1] α,β-Unsaturated acid[2] (10 mmol), CuCl (1 mmol) and tertiary butyl nitrite (20 mmol) and CH_3CN (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_2O 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).



12d

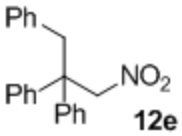
Sticky oil, 70%

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.96 (s, 3H), 5.10 (s, 2H), 7.16-7.34 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 25.56, 52.25, 66.63, 80.78, 127.97, 128.20, 128.56, 136.12, 154.64.

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

HRMS (ESI): *m/z* calcd. for $C_{15}H_{15}NNaO_2$ $(M + Na)^+$ 264.0995; found: 264.0992.



12e

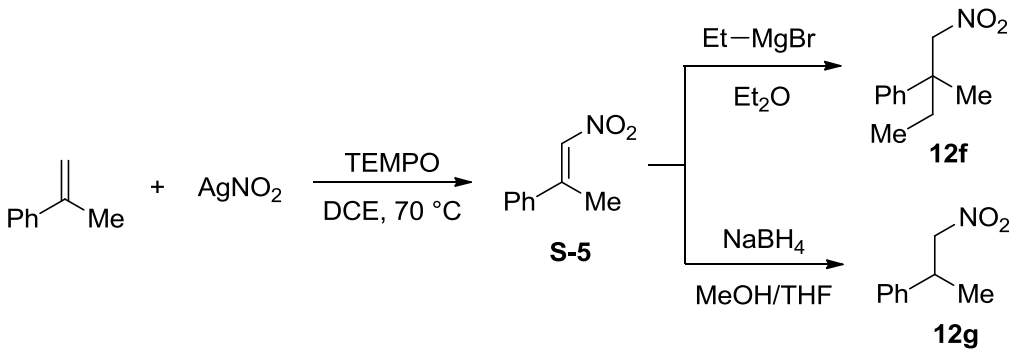
White solid, 80%

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 2H), 5.05 (s, 2H), 6.74 (d, *J* = 7.2 Hz, 2H), 7.03-7.32 (m, 13H).

^{13}C NMR (400 MHz, $CDCl_3$): δ 42.60, 51.48, 80.95, 126.80, 127.23, 127.83, 127.96, 128.31, 131.07, 136.04, 143.73.

IR (neat): 3024, 1550, 1493, 1447, 1376, 755, 698 cm^{-1}.

HRMS (ESI): *m/z* calcd. for $C_{21}H_{19}NNaO_2$ $(M+Na)^+$ 340.1308; found 340.1304.

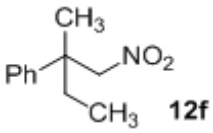


Scheme S-5. Preparation of nitroalkane **12f**/**12g**.

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 ºC 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_2O 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 $MgSO_4$, solvent removal and column purification (Hexane/EA= 1/5).



12f

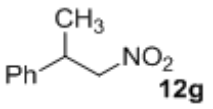
Sticky oil, 70%.

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{11}H_{15}NNaO_2$ $(M + Na)^+$ 216.0995; found: 216.0993.



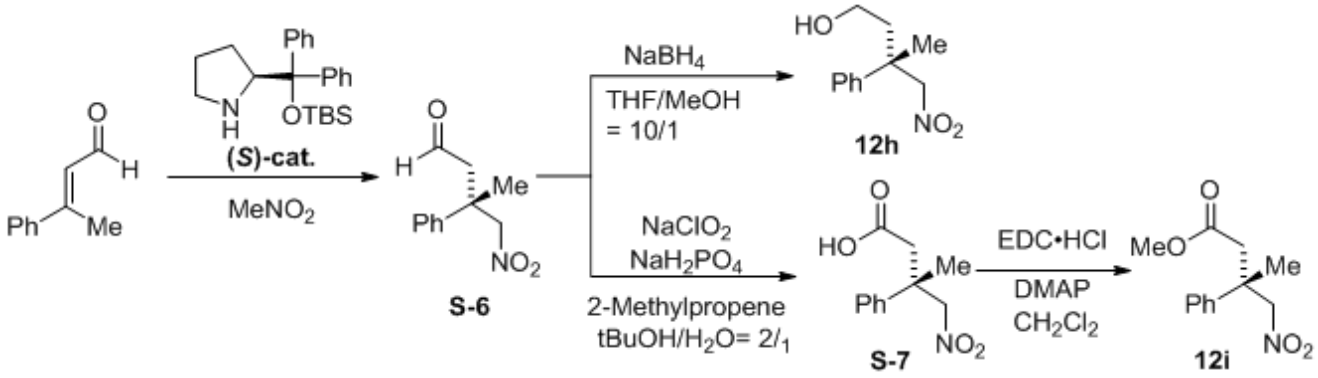
12g

To a solution of **S-5** (5 mmol) in THF/MeOH = 10/1 (20 mL) at 0 °C under argon, was added $NaBH_4$ (0.38 g, 10 mmol) slowly. After stirring for 20 min, the reaction was treated with 1N HCl and extracted with Et_2O three times. The combined organic layers were washed with brine (30 mL), dried ($MgSO_4$), 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.

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ 18.71, 38.63, 81.85, 126.89, 127.56, 128.96, 140.86.

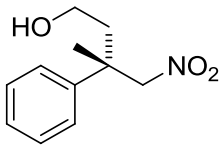
IR (neat): 2973, 1552, 1383, 1022, 766, 701 cm^{-1}.



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%).



sticky oil.

^{1}H 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).

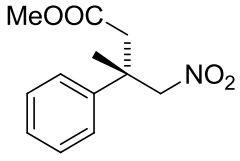
^{13}C NMR (100 MHz, $CDCl_3$): δ 22.94, 41.34, 42.00, 58.94, 85.96, 125.86, 127.28, 128.81, 141.87.

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

HRMS (ESI): *m/z* calcd. for $C_{11}H_{15}NNaO_3$ $(M + Na)^+$ 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 NaH_2PO_4•$2H_2O$ (4 mmol) were added, before adding $NaClO_2$ (6 mmol in 5 mL H_2O) slowly at 0 °C. The mixture was stirred for 1.5 h and the reaction was quenched by the addition of saturated aqueous $NaHCO_3$, 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 $MgSO_4$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_2Cl_2 (10 mL) and MeOH (0.5 mL) was added. The reaction mixture was cooled to 0ºC and EDC•HCl (2 mmol) was added, followed by DMAP (0.4 mmol). The reaction was quenched with *sat.* NH_4Cl solution after 12h, extracted with CH_2Cl_2 and the combined organic phases were dried over anhydrous $MgSO_4$, filtered and evaporated to afford the crude product, which was purified by silica gel chromatography (Hex/EA = 5/1).



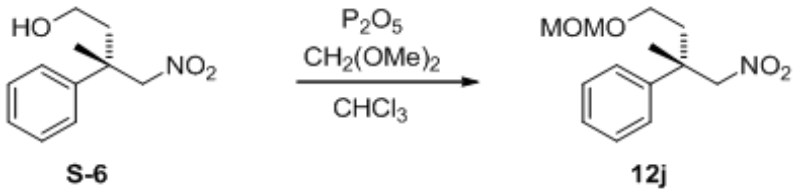
Sticky oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 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}C NMR (100 MHz, $CDCl_3$): δ 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}.

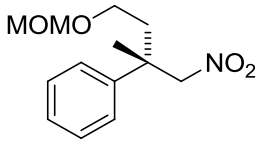
HRMS (ESI): *m/z* calcd. for $C_{12}H_{15}NNaO_4$ $(M + Na)^+$ 260.0893; found: 260.0903.



S-6 **12j**

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_2O_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}H NMR (400 MHz, $CDCl_3$): δ 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).

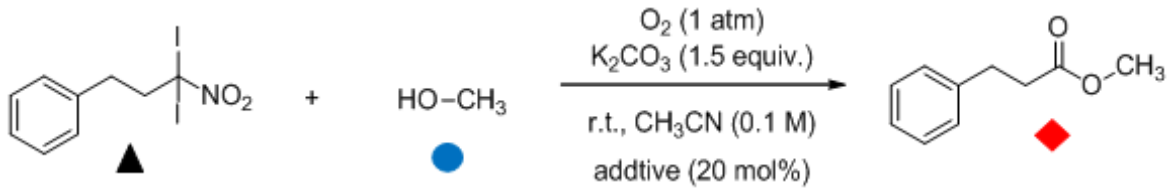
^{13}C NMR (100 MHz, $CDCl_3$): δ 22.79, 39.40, 41.37, 55.23, 63.81, 86.03, 96.38, 125.89, 127.22, 128.74, 141.82.

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.



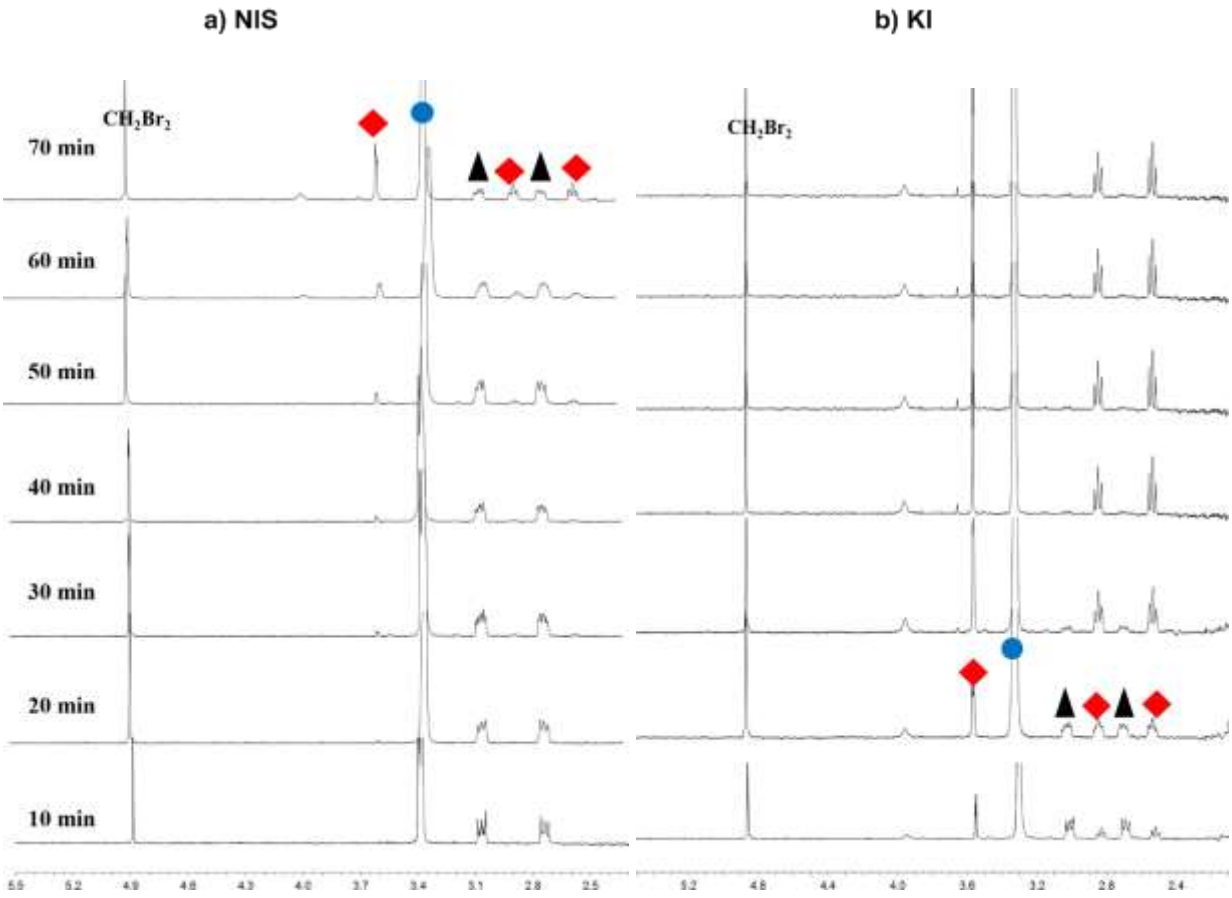


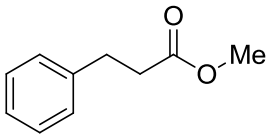
Figure S-1. Comparision by ^{1}H NMR showing reaction characters: **a**) with NIS (20 mol%); **b**) with 20 mol% KI (20 mol%).

Procedure: To a 10 mL reaction tube, α,α-diiodonitroalkane **4-2a** (0.4 mmol) and dry CH_3CN (4 mL, pre-saturated with O_2) were mixed and put under an O_2-balloon atmosphere. After

CH_2Br_2 (0.4 mmol) was added as internal standard, MeOH (2.0 mmol) and K_2CO_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 $CDCl_3$ (600 μL) for ^1H NMR analysis, wherein the yield of ester was assayed by ^1H NMR integration based on the internal standard (CH_2Br_2). See next page for sample spectra.

3.2 React IR analysis

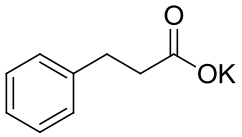
Procedure: To a reaction flask (10 mL), α,α-diiodonitroalkane **2a** (0.3 mmol), K_2CO_3 (0.15 mmol) and dry CH_3CN (6 mL, pre-saturated with O_2) were mixed and put under an O_2-balloon atmosphere. The react IR probe was inserted into the solution. After all yellow solid dissolved in CH_3CN, MeOH (1.5 mmol, 5.0 equiv.) was added at r.t. under fast, but smooth stirring. Finally, I_2 or NEt_4I was added in one portion and IR spectra were recorded every minute. After the reaction finished, $CHCl_3$ was added and the precipitate formed was filtered, collected and washed with $CHCl_3$, dissolved in D_2O and then checked by NMR directly. The collated organic solution was washed with *sat.* $Na_2S_2O_3$, dried over anhydrous magnesium sulfate, and then evaporated *in vacuo* to give the ester **6** without further purification.

Product in organic phase: 

^1H NMR (400 MHz, $CDCl_3$): δ 2.62 (t, *J* = 8.0 Hz, 2H), 2.94 (t, *J* = 8.0 Hz, 2H), 7.18-7.30 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 30.92, 35.68, 51.60, 126.25, 128.25, 128.49, 140.49, 173.33.

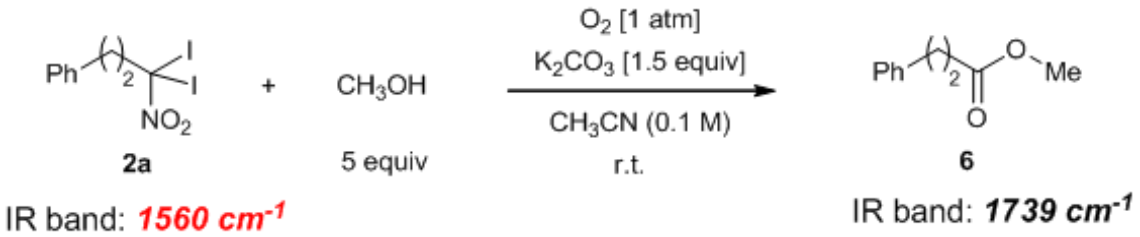
HRMS (ESI): *m/z* calcd. for $C_{10}H_{12}NaO_2$ $[M+Na]^+$ 187.0730; found:187.0716.

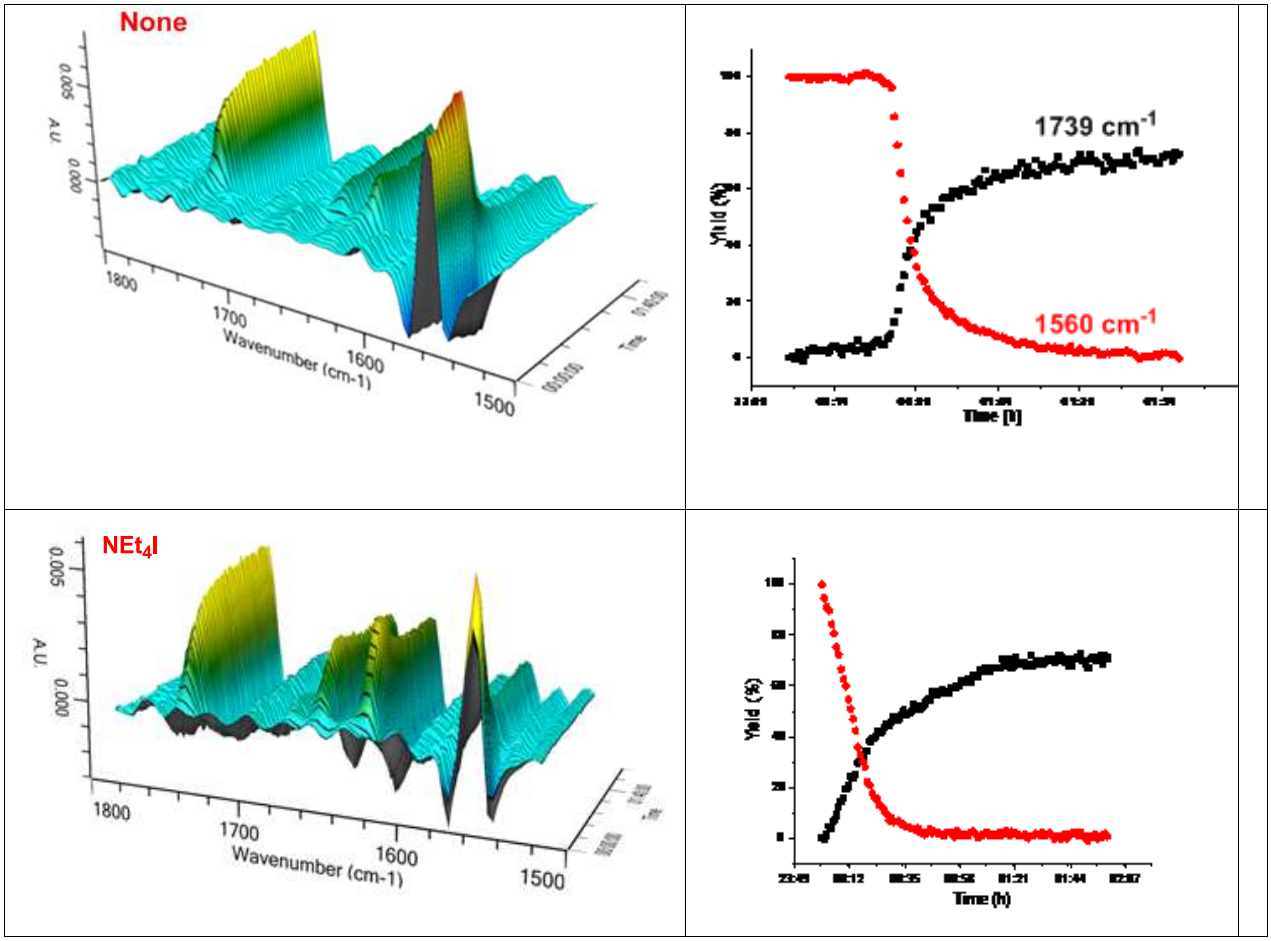
Product in water phase: 

(The data is consistent with $PHCH_2CH_2COOH$ mixed with KOH in D_2O)

^{1}H NMR (400 MHz, D_2O): 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.





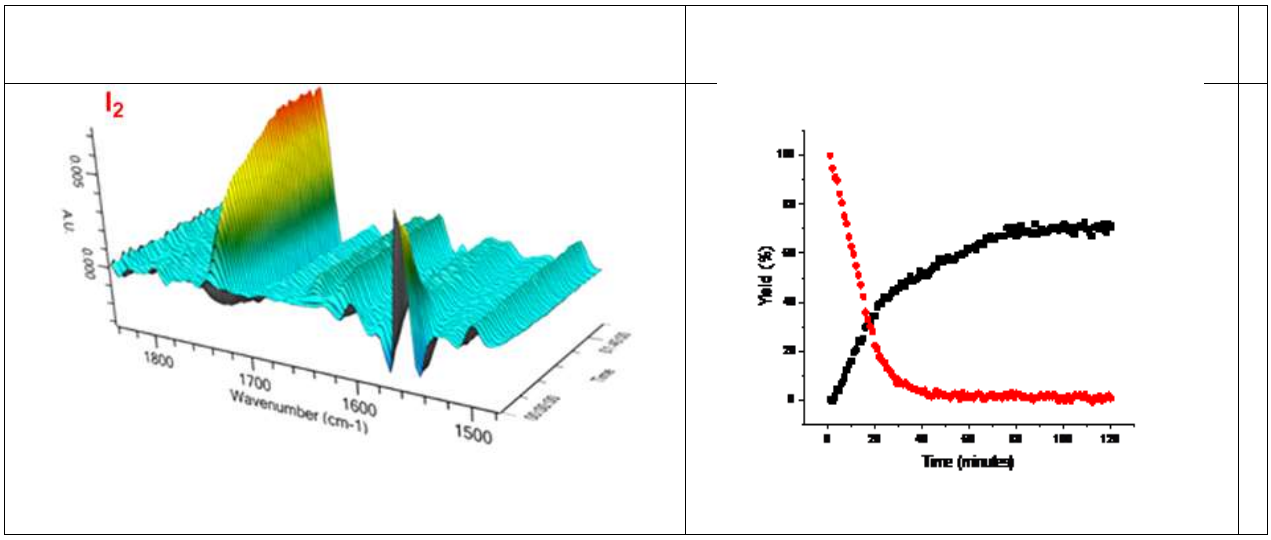
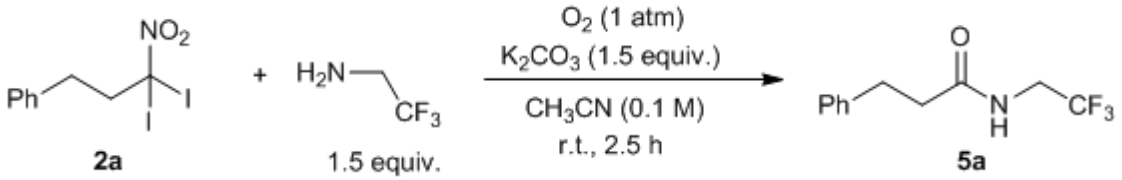


Figure S-2. React IR study of α,α-diiodonitroalkane **2a** reacting with MeOH with different additives.

4. Kinetic study of α,α-diiodonitroalkane 2a with $CF_3CH_2NH_2$.

Procedure: To a 10 mL reaction tube, α,α-diiodonitroalkane **2a** (0.4 mmol) and dry CH_3CN (4 mL, pre-saturated with O_2) were mixed and put under an O_2-balloon atmosphere. CH_2Br_2 (0.4 mmol) was added as internal standard. After this preparation, $CF_3CH_2NH_2$ (0.6 mmol) and K_2CO_3 (0.6 mmol) were added at r.t. under fast, but smooth stirring. Every 10 minutes, 100 μL of reaction mixture was removed, diluted with $CDCl_3$ (600 μL), and the yield of the amide product **5a** assayed by ^1H NMR integration based on the internal standard (CH_2Br_2).



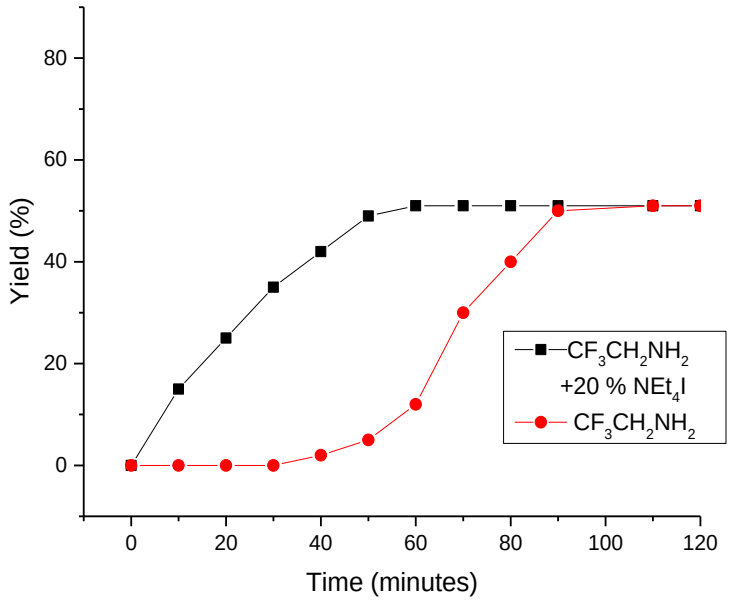
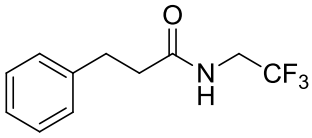


Figure S-3. ^{1}H NMR study of α,α-diidonitroalkane **2a** reacting with $CF_3CH_2NH_2$.



White solid, yield = 50%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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 $C_{11}H_{12}F_3NNaO$ $(M + Na)^+$ 254.0763; found 254.0765.

5. ^{1}H NMR study of benzylamine with α,α-diiodnitroalkane 2a.

5.1 ^{1}H NMR investigation of the reaction of α,α-diiodnitroalkane 2a and benzylamine

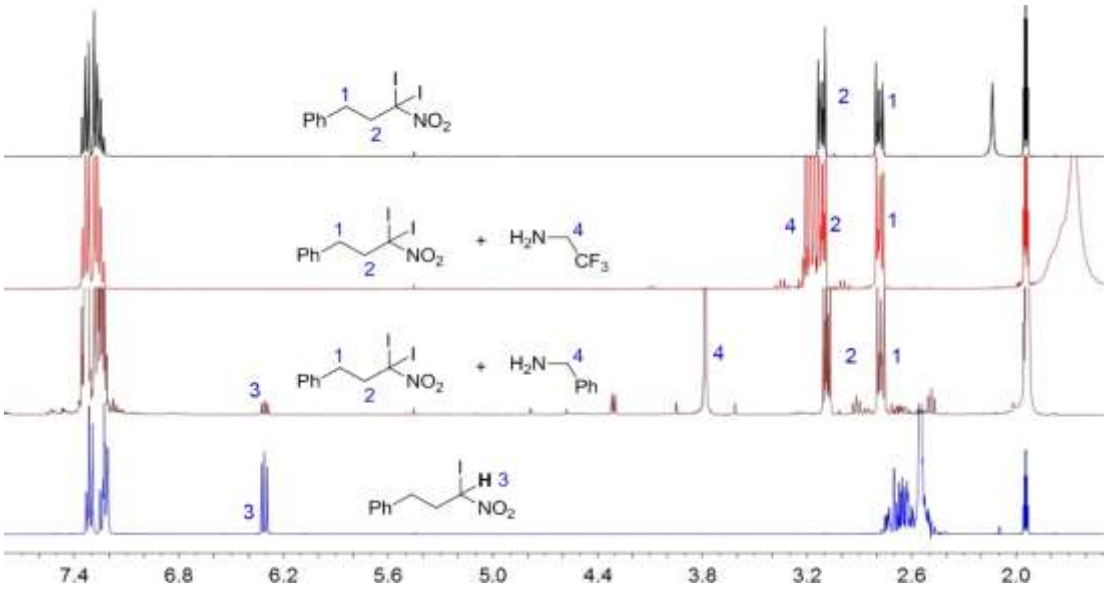
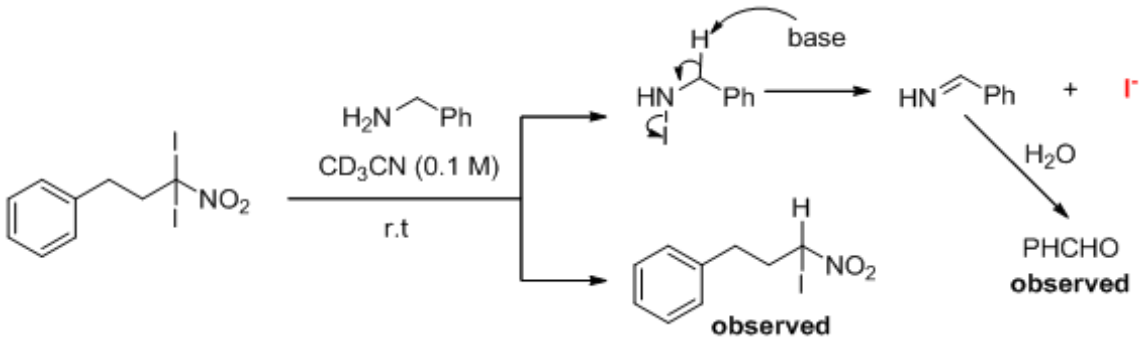


Figure S-4. ^{1}H NMR study at r.t.



Scheme S-8. Proposed reaction mechanism for I⁻ generation.

Immediately after α,α-diiodnitroalkane **2a** was mixed with benzylamine (1.5 equiv) in CD_3CN 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 benzylaldhyde. We thus propose a side reaction as given in Scheme S-8. However, when $CF_3CH_2NH_2$ was used instead of benzylamine, this side reaction was not observed (*cf.* red and purple spectrums).

5.2 Kinetic study of benzylamine with α,α-diiodnitroalkane 2a using ^{1}H NMR.

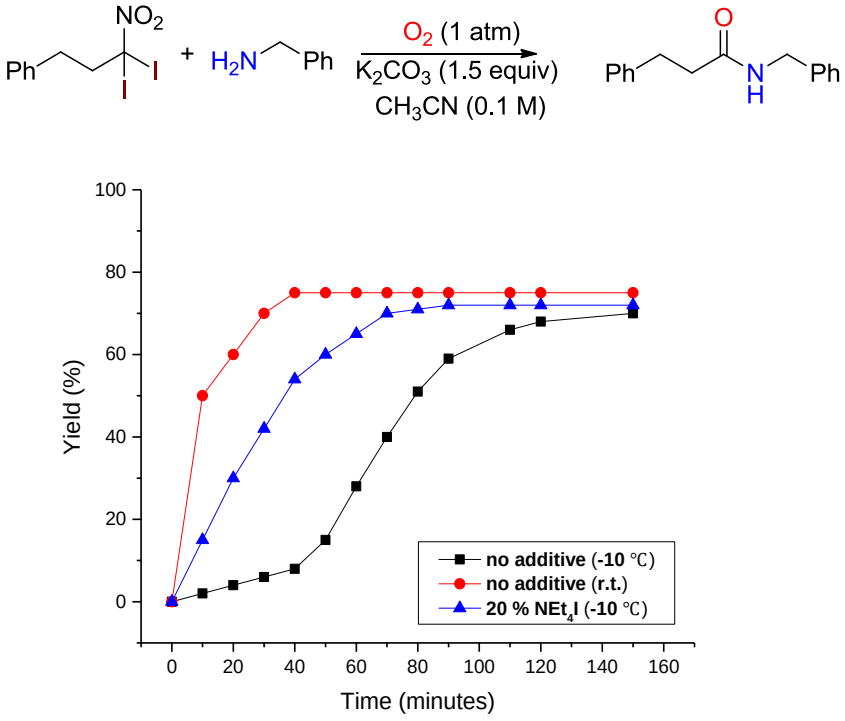
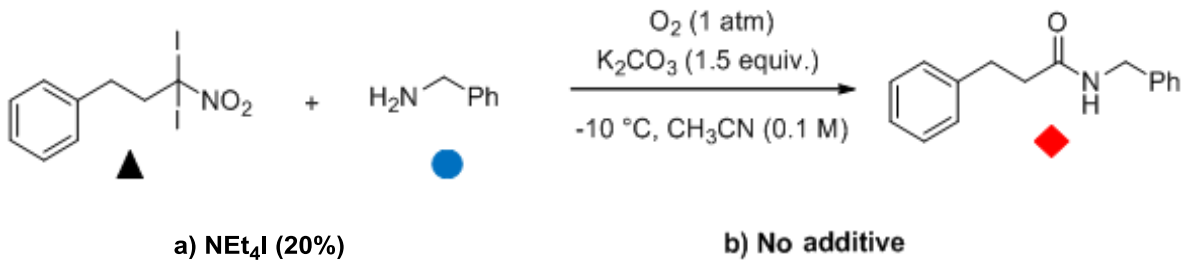


Figure S-5. ^{1}H NMR study of benzylamine with α,α-diidonitroalkane **2a**

Procedure: To a 10 mL reaction tube, α,α-diiodonitroalkane **2a** (0.4 mmol), dry CH_3CN (4 mL, pre-saturated with O_2) were mixed and put under an O_2-balloon atmosphere. CH_2Br_2 (0.4 mmol) was added as an internal standard. After this preparation, $PhCH_2NH_2$ (2.0 mmol) and K_2CO_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}H NMR spectroscopy.



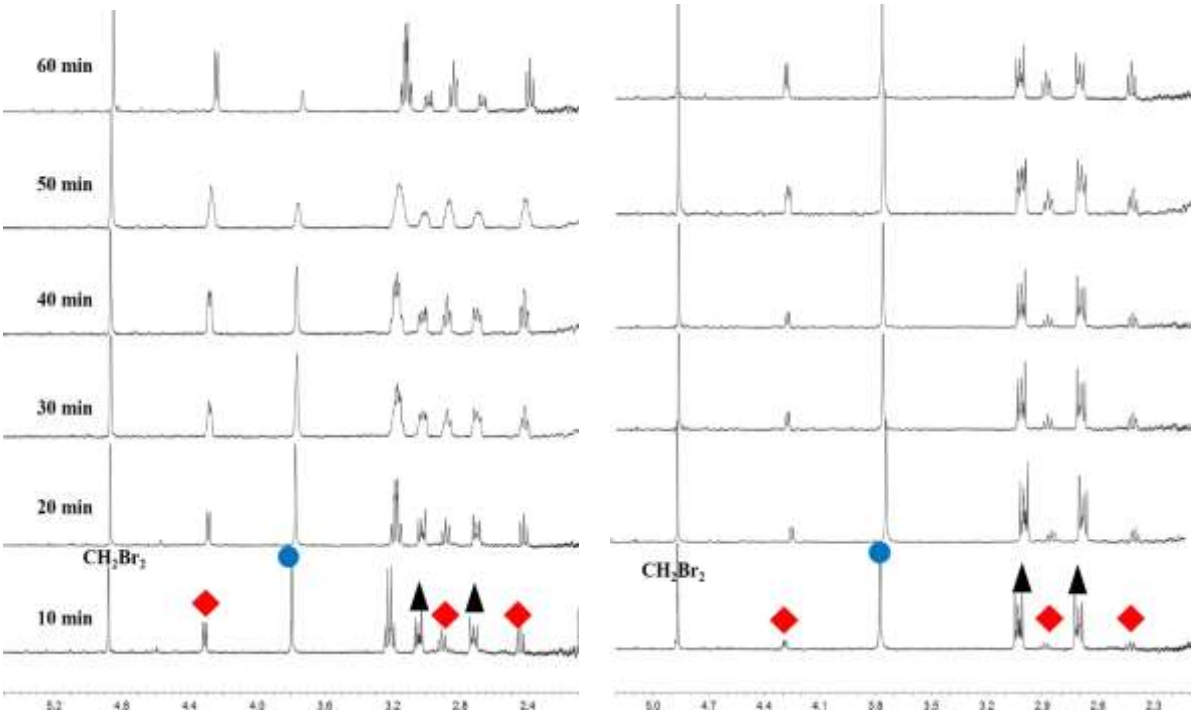
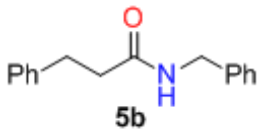


Figure S-6. Comparision of the effect of I^- at -10 °C during oxidative amide formation.



5b

White solid, yield = 75%.

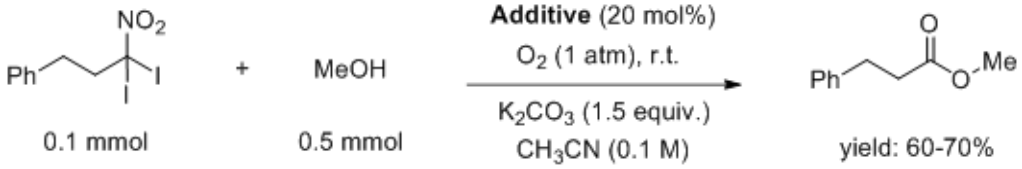
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (t, *J* = 7.6 Hz, 2H), 2.96 (t, *J* = 7.6 Hz, 2H), 3.45 (d, *J* = 5.6 Hz, 2H), 5.95 (br s, 1H), 7.11-7.30 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 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



Additive (20 mol%)	Temp. (°C)	Induction time (min)
none	25	50–60
	50	8–10
PPh_3	25	< 5
SMe_2	25	< 5
^{t}BuOOH	25	< 5
AIBN	25	50–60
	50	8–10
BPO	25	50–60
	50	13–15
TEMPO	25	30–40

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), K_2CO_3 (0.15 mmol), dry CH_3CN (6 mL, pre-saturated with O_2) and an O_2-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/CH_2Cl_2 = 1/1) and by observing the color changes (Figure S-5).

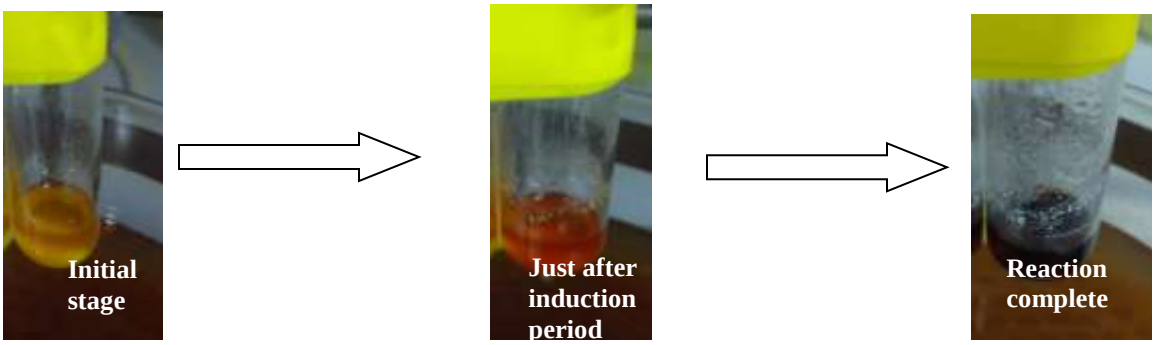


Figure S-7. Color change of the reaction at 50 °C (oil bath) without any additive.

7. Optimization, formation and characterization of esters.

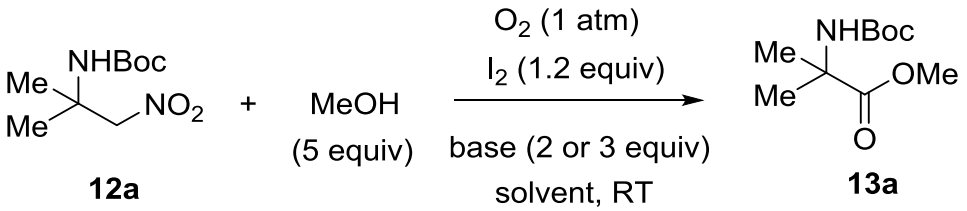


Table S1. Optimization of Oxidative Esterification Process.[a]

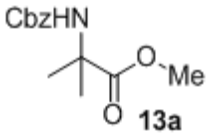
Entry	Base	Solvent	Time [h]	Yield [%]
1	K_2CO_3	CH_3CN	24h	trace
2	K_2CO_3	THF	24 h	trace
3	K_2CO_3	CH_2Cl_2	24 h	trace
4[b]	K_2CO_3	MeOH	6 h	71
5[b]	Li_2CO_3	MeOH	6 h	62
6[b]	Na_2CO_3	MeOH	12h	49
7[b]	Cs_2CO_3	MeOH	1h	22
8[b]	NaOMe	MeOH	1h	41
9[b]	KOMe	MeOH	1h	59
10[b,c]	KOMe	MeOH	1h	71

[a] Reactions were conducted with nitroalkane **12a** (0.2 mmol), MeOH (1.0 mmol), base (0.4 mmol) under O_2 atmosphere in CH_3CN (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 α-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.* $Na_2S_2O_3$ 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**).



13a

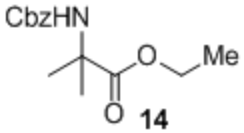
Sticky oil, yield = 70%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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.



14

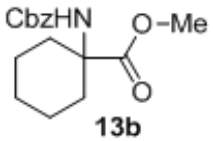
Sticky oil, yield = 60%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 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}C NMR (100 MHz, $CDCl_3$): δ 14.03, 25.01, 56.42, 61.54, 66.45, 128.04, 128.07, 128.48, 136.42, 174.56.

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

HRMS *m/z* calcd. for $C_{14}H_{20}NO_4$ $(M + H)^+$ 266.1387; found: 266.1392.



13b

Sticky oil, yield = 65%.

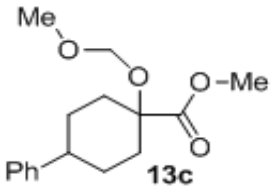
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24-1.33 (m, 1 H), 1.39-1.49 (m, 2H), 1.59-1.63 (m, 3H), 1.80-1.87 (m, 2H), 1.98-2.02 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 3.66 (br s, 3H), 4.95 (br s, 1H), 5.07 (s, 2H), 7.28-7.36 (5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 21.20, 25.11, 32.60, 52.28, 59.11, 66.67, 128.05, 136.37, 155.19, 174.82.

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

HRMS *m/z* calcd. for $C_{16}H_{21}NNaO_4$ $(M + Na)^+$ 314.1363; found: 314.1365.



13c

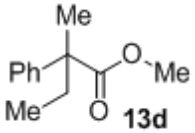
Sticky oil, yield = 68%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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.



13d

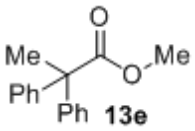
Sticky oil, yield = 60%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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.



13e

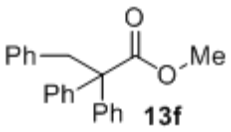
White solid, yield = 75%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93 (s, 3H), 3.73 (s, 3H), 7.20-7.32 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 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 $C_{16}H_{16}NaO_2$ $(M + Na)^+$ 263.1043; found: 263.1042.



13f

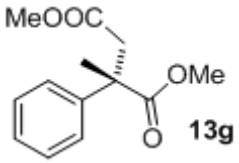
White solid, yield = 79%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 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}C NMR (100 MHz, $CDCl_3$): δ 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 $C_{22}H_{20}NaO_2$ (M + Na)+ 339.1356; found: 339.1355.



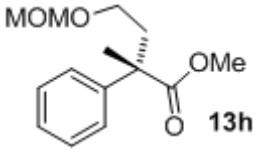
13g

Yield = 72%, sticky oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68 (s, 3H), 2.80 (d, *J* = 16.4 Hz, 1H), 3.26 (d, *J* =16.4 Hz, 1H), 3.63 (s, 3H), 3.68 (s, 3H), 7.22-7.34 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ23.35, 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 : $C_{13}H_{16}NaO_4$ $(M + Na)^+$ 259.0941; found: 259.0944.



13h

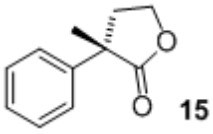
Yield = 70%, sticky oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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.



15

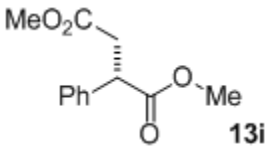
Yield = 80%, sticky oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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 C11H12NaO2 $(M + Na)^+$ 199.0730; found: 199.0732.



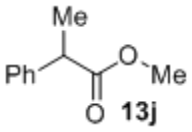
13i

K_2CO_3 used instead of KOMe. Sticky oil, yield = 60%.

The NMR data is consistent with previous report[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 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, 10Hz, 1H), 7.23-7.33 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 37.60, 47.06, 51.85, 52.35, 127.66, 127.70, 128.87, 137.63, 171.96, 173.41.



13j Sticky oil, yield = 61%

^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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}.

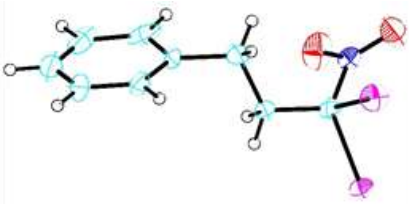
HRMS (ESI): *m/z* calcd. for $C_{10}H_{12}NaO_2$ $(M+Na)^+$187.0730; Found 187.0727.

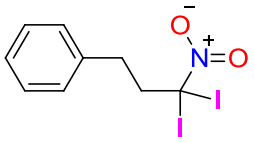
HRMS (ESI): *m/z* calcd. for $C_{12}H_{14}NaO_4$ $(M + Na)^+$ 245.0784; found: 245.0788.

8. X-Ray structure of α,α-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 $C_9H_9I_2NO_2$ 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 = 54.0o and f = 120.0o. The exposure rate was 12.0 [sec./o]. The detector swing angle was 30.00o. Another sweep was performed using w scans from –60.0 to 120.0o in 1.00o step, at c = 54.0o and f = 240.0o. The exposure rate was 12.0 [sec./o]. The detector swing angle was 30.00o. Another sweep was performed 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 30.20o. Another sweep was performed using w scans from –60.0 to 120.0o in 1.00o step, at c = 54.0o and f = 120.0o. The exposure rate was 12.0 [sec./o]. The detector swing angle was 30.20o. Another sweep was performed using w scans from –60.0 to 120.0o in 1.00o step, at c = 54.0o and f = 240.0o. The exposure rate was 12.0 [sec./o]. The detector swing angle was 30.20o. 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

Empirical Formula	$C_{9}H_{9}I_{2}NO_{2}$
Formula Weight	416.98
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.400 X 0.400 X 0.300 mm
Crystal System	orthorhombic
Lattice Type	Primitive

Lattice Parameters	a = 12.08000 Å
	b = 11.70400 Å
	c = 16.18200 Å
	V = 2287.88107 $Å^3$
Space Group	Pbca (#61)
Z value	8
D_{calc}	2.421 g/cm^3
F_{000}	1536.00
m(MoKa)	54.758 cm^{-1}

B. Intensity Measurements

Diffractometer	XtaLAB mini
Radiation	MoKα (l = 0.71075 Å)
	graphite monochromated
Voltage, Current	50kV, 12mA
Temperature	-123.0 °C
Detector Aperture	75.0 mm (diameter)
Data Images	540 exposures
ω oscillation Range (χ=54.0, ϕ=0.0)	-60.0 - 120.0°
Exposure Rate	12.0 sec./°
Detector Swing Angle	30.00°
ω oscillation Range (χ=54.0, ϕ=120.0)	-60.0 - 120.0°

Exposure Rate	12.0 sec./^{o}
Detector Swing Angle	30.00^{o}
ω oscillation Range (χ=54.0, ϕ=240.0)	-60.0 - 120.0^{o}
Exposure Rate	12.0 sec./^{o}
Detector Swing Angle	30.00^{o}
ω oscillation Range (χ=54.0, ϕ=0.0)	-60.0 - 120.0^{o}
Exposure Rate	12.0 sec./^{o}
Detector Swing Angle	30.20^{o}
ω oscillation Range (χ=54.0, ϕ=120.0)	-60.0 - 120.0^{o}
Exposure Rate	12.0 sec./^{o}
Detector Swing Angle	30.20^{o}
ω oscillation Range (χ=54.0, ϕ=240.0)	-60.0 - 120.0^{o}
Exposure Rate	12.0 sec./^{o}
Detector Swing Angle	30.20^{o}
Detector Position	50.11 mm
Pixel Size	0.073 mm
$2\theta_{max}$	55.0^{o}
No. of Reflections Measured	Total: 20398
	Unique: 2620 (R_{int} = 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	$\Sigma\ w\ (Fo^2 - Fc2)2$
Least Squares Weights	$\omega = 1/\ [\ s^2(Fo2) + (0.0820\ .\ P)2$ $+ 55.3747\ .\ P\ ]$ where $P = (Max(Fo^2,0) + 2Fc2)/3$
2θmax cutoff	55.0^o
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: ωR2 (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 $B_{iso/Beq}$

atom	x	y	z	B_{eq}
I1	-0.05195(7)	1.16338(7)	0.13541(5)	2.46(2)
I2	0.17729(8)	1.09930(8)	0.26361(6)	3.22(2)
O7	-0.0352(10)	0.9763(10)	0.3179(6)	4.1(2)
O8	-0.0882(10)	0.8909(10)	0.2095(8)	4.4(2)
N3	-0.0307(9)	0.9582(9)	0.2457(7)	2.62(18)
C6	0.0486(10)	1.0264(10)	0.1891(8)	2.32(19)
C12	0.1920(9)	0.7723(10)	0.0811(7)	2.20(19)
C13	0.0936(10)	0.9522(10)	0.1211(7)	2.19(18)
C14	0.1208(11)	0.6827(11)	0.0630(11)	3.4(3)
C15	0.1427(14)	0.6131(12)	-0.0079(11)	3.7(3)
C16	0.2356(15)	0.6333(13)	-0.0530(9)	4.0(3)
C17	0.3065(12)	0.7200(13)	-0.0327(9)	3.3(2)
C18	0.2842(11)	0.7897(10)	0.0347(8)	2.6(2)
C19	0.1619(14)	0.8498(13)	0.1520(8)	3.5(3)

$B_{eq} = 8/3\ p^{2}(U_{11(aa^*)}{}^{2} + U_{22(bb^*)}{}^{2} + U_{33(cc^*)}{}^{2} + 2U_{12(aa^*bb^*)}\cos g + 2U13(aa^*cc^*)\cos b + 2U23(bb^*cc^*)\cos a)$

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

atom	x	y	z	B_{iso}
H13A	0.14067	0.99951	0.08454	2.628
H13B	0.03095	0.92332	0.08760	2.628

H14	0.05848	0.66772	0.09711	4.065
H15	0.09318	0.55365	-0.02311	4.485
H16	0.25146	0.58650	-0.09947	4.791
H17	0.37121	0.73246	-0.06483	3.979
H18	0.33369	0.84989	0.04843	3.095
H19A	0.23022	0.87762	0.17909	4.186
H19B	0.11848	0.80646	0.19336	4.186

Table 3. Anisotropic displacement parameters

atom	U_{11}	U22	U33	U12	U13	U23
I1	0.0337(5)	0.0280(4)	0.0316(4)	0.0096(3)	-0.0029(3)	0.0017(3)
I2	0.0401(6)	0.0399(5)	0.0425(6)	-0.0048(4)	-0.0068(4)	0.0006(4)
O7	0.062(7)	0.057(7)	0.036(5)	-0.013(6)	0.008(5)	-0.004(5)
O8	0.044(6)	0.053(7)	0.070(7)	-0.019(5)	0.007(6)	-0.017(6)
N3	0.040(6)	0.027(5)	0.032(5)	0.008(5)	0.001(4)	0.000(4)
C6	0.029(6)	0.027(6)	0.032(6)	0.012(5)	-0.007(5)	0.001(5)
C12	0.027(5)	0.032(6)	0.025(5)	0.018(4)	0.002(4)	0.001(4)
C13	0.031(6)	0.028(6)	0.024(5)	0.007(5)	0.000(4)	0.001(4)
C14	0.031(6)	0.026(6)	0.072(10)	0.009(5)	0.003(6)	0.015(6)
C15	0.054(9)	0.025(6)	0.063(9)	0.005(6)	-0.012(8)	-0.007(6)
C16	0.071(11)	0.039(7)	0.042(8)	0.019(8)	-0.014(7)	-0.013(6)
C17	0.040(7)	0.042(8)	0.044(7)	0.013(6)	0.012(6)	0.000(6)
C18	0.035(6)	0.020(5)	0.042(7)	-0.001(5)	0.005(5)	-0.002(5)

C19	0.056(9)	0.047(8)	0.029(6)	0.026(7)	0.003(6)	0.005(6)

The general temperature factor expression: $exp(-2p^2(a^{*2}U_{11h}^2 + b^{*2}U_{22k}^2 + c^{*2}U_{33l}^2 + 2a^*b^*U_{12hk} + 2a^*c^*U13hl + 2b^*c^*U23kl))$

Table 4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
I1	C6	2.191(12)	I2	C6	2.145(12)
O7	N3	1.188(15)	O8	N3	1.202(16)
N3	C6	1.547(16)	C6	C13	1.503(17)
C12	C14	1.387(18)	C12	C18	1.359(17)
C12	C19	1.507(18)	C13	C19	1.54(2)
C14	C15	1.43(2)	C15	C16	1.36(2)
C16	C17	1.37(2)	C17	C18	1.389(19)

9. References

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