

Supporting Information for:

Consecutive Oxygen-based Oxidations Convert Amines to α -Cyanoepoxides

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General information. All commercially available compounds and solvents (Acros, Aldrich, Fluka, Alfa Aesar and Merck) were used without purification. TPP (5,10,15,20-tetraphenyl-21*H*,23*H*-porphine, low chlorine) was purchased from Alfa Aesar (A18261). HPLC grade THF (Tetrahydrofuran) was purchased from VWR. The Vapourtec R-2+ model pump was used for the continuous flow synthesis with a solution flow rate of 2 mL/min. Via an ETFE T-mixer (IDEX Health and Science) the substrate solution was mixed with oxygen (99.995%, H₂O <3.0 ppm/mol; ALPHAGAZ™ 1 O₂; Werk DEF 2 Krefeld-Gellep), which was delivered through a check valve from an oxygen gas tank. Gas pressure was regulated to 20 bar and the flow adjusted to 15 mL/min with a gas-flow controller (Influx, SV1B5-AI05). This solution was then pumped through the 7.5 mL photoreactor, consisting of fluorinated ethylene-propylene copolymer (FEP) tubing (IDEX Health and Science, natural color, 1.57 mm outer diameter, 0.76 mm inner diameter) wrapped around a glass plate (7×9 cm²) in two layers. A 30 cm piece of tubing was used for the connection of the T-mixer with a photoreactor. A 0.5 mL precooling loop covered with aluminum foil was placed additionally in the bath before the photoreactor. The LED module (OSA Opto Light, OLM-018 B, 420 nm emission wavelength, 72 W; power supply Manson HCS-3202) was mounted in front of this plate at a distance of 3 cm. The photoreactor was immersed in an acetone bath (for reactions at –60 °C) which was cooled using an immersion cooler (Huber, TC100E-F-NR). For reactions at room temperature, the photoreactor was suspended in a water bath. A piece of FEP tubing (30 cm) was used for the connection of the outlet of photoreactor to a 7 bar back pressure regulator (average pressure in a system was around 9 bar). The residence time in the photoreactor was measured to be 2.5 minutes. Concentration on the rotary evaporator was performed immediately after addition of the malonic acid derivative ($T_{\text{water bath}} = 30\text{ °C}$; automatic vacuum control). When all solvent was visually removed, the vacuum strength was increased (pump down to 5 mbar) and pumping was continued for an additional 5 minutes. Macherey-Nagel silica gel 60M (0.04–0.063 mm) was used for the dry loading of the column after concentration in vacuo. All compounds unless described otherwise were purified using a Reveleris® X2 flash chromatography system (Grace Discovery Science) with a commercially

available (Reveleris) column: Silica 40g, 40 μm with a flow rate of eluent 40 mL/min. ELSD and UV (254 and 280 nm) detectors were used with low detector sensitivity at 20 mV and 0.05 AU threshold detection, respectively. All fractions were collected after TPP (intensive violet color) came out from the column. The compounds were visualized by UV₂₅₄ light and the chromatography plates (Merck, Silica gel 60 F₂₅₄) were developed with an aqueous solution of potassium permanganate, prepared from 2.5 g KMnO₄ and 12.5 g Na₂CO₃ in 250 mL water. Chromatographic columns were reused after washing with acetone/methanol (from 100:0 to 95:5 over 7.5 column volumes). ¹H and ¹³C NMR spectra were obtained using a Varian 400 and 100 MHz MR System respectively, are reported in parts per million (ppm) relative to residual solvent peaks (δ), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets), with coupling constants (*J*) in Hertz (Hz) and integration. Chemical shifts are calibrated to the residual proton and carbon resonance of the solvent: CDCl₃ (¹H: 7.26, ¹³C: 77.16), CD₃OD (¹H: 3.31, ¹³C: 49.00).¹

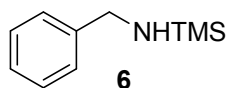
¹ H. E. Gottlieb, V. Kotlyar, and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512.

Formation of the alkene upon reaction of methyl cyanoacetate with *N*-benzylidene-1-phenylmethanamine, as prepared by classical condensation

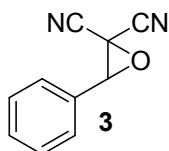
For the peroxide free deamination Mannich-type coupling, *N*-benzyl-phenylaldimine was prepared from benzylamine and benzaldehyde² as described below. A 0.1M solution in THF of the imine was treated with 1.2 equiv of methyl cyanoacetate. TLC (Hexane/EtOAc 3:1) showed the immediate formation of the corresponding alkene. NMR after concentration in vacuo showed a mixture of starting imine and alkene in ratio 0.7:1.0.

Preparation of peroxide-free (E)-N-benzylidene-1-phenylmethanamine. Water -free MgSO₄ (10 g) was added to 120 mL dichloromethane, followed by the addition of benzylamine (**1**) (6.0 g, 56.0 mmol) and benzaldehyde (6.0 g, 56.6 mmol) at room temperature. The resulted suspension was stirred for 3 days before it was filtered and concentrated under reduced pressure. The residue was purified by vacuum distillation to give *N*-benzyl-phenylaldimine (7.8 g, 74%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): 4.78 (s, 2H), 7.20–7.40 (m, 8H), 7.75–7.78 (m, 2H), 8.40 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): 64.9, 126.9, 127.9, 128.1, 128.5, 130.5, 136.0, 139.2, 161.9. The NMR data were in complete agreement with earlier reports.²

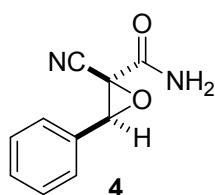
² Y. Zhang, Z. Lu, A. Desai, and W. D. Wulff, *Org. Lett.*, 2008, **10**, 5429.



N-Benzyl-1,1,1-trimethylsilanamine (6). Sulfuric acid (one drop) was added to a stirred solution of benzylamine **1** (19.4 mL, 178 mmol) and hexamethyldisylazane (20.5 mL, 98 mmol) at room temperature. The resulted mixture was stirred for 3 h at 170 °C, followed by vacuum distillation to afford silylamine **6** (24.6 g, 77%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): 0.23 (s, 9H), 0.91 (br.s., 1H), 4.06 (s, 2H), 7.33–7.44 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): 0.2, 46.1, 126.5, 127.0, 128.3, 144.4. The NMR data were in complete agreement with reported earlier.³

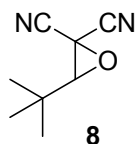


3-Phenyloxirane-2,2-dicarbonitrile (3). **From benzylamine (1):** TPP (7 mg) was added to a solution of benzylamine **1** (0.55 mL, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at –60 °C. When the collection was finished, malononitrile (0.56 g, 8.5 mmol) was added and the solution was concentrated under reduced pressure. The residue was loaded on silica (1 g) and purified (eluent: hexane/EA from 98:2 to 95:5 over 20 column volumes) to give epoxide **3** (0.63 g, 74%) as a colorless oil. **From mono-TMS benzylamine 6:** TPP (7 mg) was added to a solution of mono-TMS benzylamine (**6**) (0.90 g, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at room temperature. When the collection was finished, malononitrile (0.56 g, 8.5 mmol) was added and the solution was concentrated under reduced pressure. The residue was loaded on silica (1.5 g) and purified (eluent: hexane/EA from 98:2 to 95:5 over 20 column volumes) to give epoxide **3** (0.59 g, 69%) as a colorless oil. R_f = 0.7 (hexane/ethyl acetate 4:1); ^1H NMR (400 MHz, CDCl_3): 4.71 (s, 1H), 7.42–7.56 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): 41.7, 65.8, 110.2, 111.7, 126.8, 127.5, 129.1, 131.4; $[\text{M}+\text{Na}+\text{MeOH}]^+$ calcd for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{NaO}_2$ 225.0640, found 225.0648.

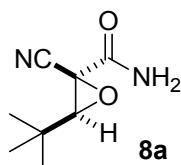


³ M. J. Barany, R. P. Hammer, R. B. Merrifield, and G. Barany, *J. Am. Chem. Soc.*, 2005, **127**, 508.

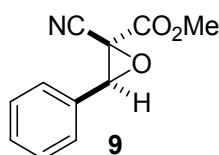
(2*R*,3*S*)-2-Cyano-3-phenyloxirane-2-carboxamide (4). An increase of the ethyl acetate ratio (to 100% over 20 columns) was used to isolate amide **4** (90 mg, 10%) from the reaction mixture above as white crystals. $R_f = 0.2$ (hexane/ethyl acetate 2:1); ^1H NMR (400 MHz, CD_3OD^4): 4.58 (s, 1H), 7.45 (br.s., 5H); ^{13}C NMR (100 MHz, CD_3OD): 56.7, 65.3, 114.7, 127.6, 129.6, 131.1, 132.1, 166.4; HRMS (EI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{10}\text{H}_8\text{N}_2\text{NaO}_2$ 211.0483, found 211.0480.



3-(*tert*-Butyl)oxirane-2,2-dicarbonitrile (8). TPP (7 mg) was added to a solution of neopentylamine **7** (0.59 mL, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at $-60\text{ }^\circ\text{C}$. When the collection was finished, malononitrile (0.56 g, 8.5 mmol) was added and the solution was concentrated under the reduced pressure. The residue was loaded onto silica (1 g) and purified (eluent: hexane/EA from 98:2 to 95:5 over 20 column volumes) to give epoxide **8** (0.42 g, 56%) as white crystals; $R_f = 0.8$ (hexane/ethyl acetate 4:1); ^1H NMR (400 MHz, CDCl_3): 1.16 (s, 9H), 3.41 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): 25.8, 32.0, 37.1, 73.4, 111.2, 112.5.

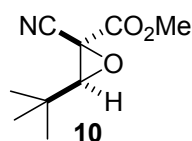


(2*R*,3*S*)-3-(*tert*-Butyl)-2-cyano-2-carboxamido-oxirane (8a). An increase of the ethyl acetate ratio (to 100% over 20 columns) was used to isolate amide **8a** (0.23 g, 28%) from the reaction mixture above as white crystals. $R_f = 0.2$ (hexane/ethyl acetate 2:1); ^1H NMR (400 MHz, CD_3OD): 1.15 (s, 9H), 3.22 (s, 1H); ^{13}C NMR (100 MHz, CD_3OD): 26.4, 32.6, 51.3, 73.1, 115.8, 167.7; HRMS (EI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_8\text{H}_{12}\text{N}_2\text{NaO}_2$ 191.0796, found 191.0791.

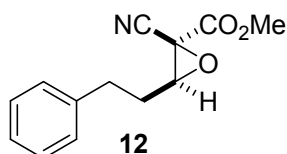


⁴ Amides **4** and **8a** were only poorly soluble in CDCl_3 , thus CD_3OD was chosen as a solvent for NMR.

(2R,3S)-Methyl 2-cyano-3-phenyloxirane-2-carboxylate (9). From benzylamine (**1**): TPP (7 mg) was added to a solution of benzylamine **1** (0.55 mL, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at -60°C . When the collection was finished, methyl cyanoacetate (0.53 mL, 6 mmol) was added and the solution was concentrated under reduced pressure. The residue was loaded onto silica (1 g) and purified (eluent: hexane/EA from 98:2 to 80:20 over 20 column volumes) to give epoxide **9** (0.72 g, 71%) as a colorless oil. **From mono-TMS benzylamine 6:** TPP (7 mg) was added to a solution of mono-TMS benzylamine **6** (0.90 g, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at room temperature. When the collection was finished, the resulting solution was treated with methyl cyanoacetate (0.53 mL, 6 mmol) followed by concentration under reduced pressure. The residue was loaded on silica (1.5 g) and purified (eluent: hexane/EA from 98:2 to 80:20 over 20 column volumes) to give epoxide **9** (0.73 g, 72%) as a colorless oil. $R_f = 0.4$ (hexane/ethyl acetate 4:1). The obtained NMR data were in complete agreement with literature reports.⁵ ^1H NMR (400 MHz, CDCl_3): 3.90 (s, 3H), 4.54 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): 53.2, 54.4, 64.5, 112.9, 126.7, 128.8, 129.7, 130.4, 163.1.

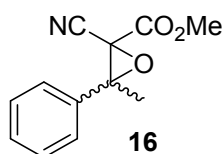


(2R,3S)-Methyl 3-(tert-butyl)-2-cyanooxirane-2-carboxylate (10). TPP (7 mg) was added to a solution of neopentylamine (**7**) (0.59 mL, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at -60°C . When the collection was finished, methyl cyanoacetate (0.53 mL, 6 mmol) was added and the solution was concentrated under reduced pressure. The residue was loaded onto silica (1 g) and purified (eluent: hexane/EA from 98:2 to 80:20 over 20 column volumes) to give epoxide **10** (0.75 g, 82%) as a colorless oil. $R_f = 0.5$ (hexane/ethyl acetate 4:1); ^1H NMR (400 MHz, CDCl_3): 1.12 (s, 9H), 3.22 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): 26.1, 31.7, 47.9, 54.3, 72.2, 114.0, 164.3; HRMS (EI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_9\text{H}_{13}\text{NNaO}_3$ 206.0793, found 206.0796.

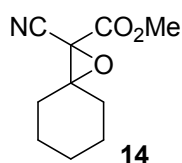


⁵ K. Motokura, N. Fujita, K. Mori, T. Mizugaki, K. Ebitani, and K. Kaneda, *J. Am. Chem. Soc.*, 2005, **127**, 9674.

(2*R*,3*S*)-Methyl 2-cyano-3-phenethyloxirane-2-carboxylate (12). TPP (7 mg) was added to a solution of 3-phenylpropylamine (**11**) (0.71 mL, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at -60°C. When the collection was finished, methyl cyanoacetate (0.53 mL, 6 mmol) was added and the solution was concentrated under the reduced pressure. The residue was loaded on silica (1 g) and purified (eluent: hexane/EA from 98:2 to 80:20 over 20 column volumes) to give epoxide **12** (0.81g, 70 %) as a colorless oil. R_f = 0.5 (hexane/ethyl acetate 4:1); ^1H NMR (400 MHz, CDCl_3): 2.17 (dd, J = 13.8, 7.6 Hz, 2H), 2.83–2.98 (m, 2H), 3.51 (dd, J = 6.0, 6.0 Hz, 1H), 3.83 (s, 3H), 7.22–7.35 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): 31.3, 31.7, 50.4, 54.2, 64.0, 113.5, 126.7, 128.4, 128.8, 139.3, 163.7; HRMS (EI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{13}\text{H}_{13}\text{NNaO}_3$ 254.0793, found 254.0820.

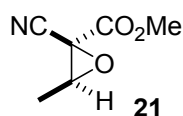


Methyl 2-cyano-3-methyl-3-phenyloxirane-2-carboxylate (16). TPP (7 mg) was added to a solution of *S*(-)- α -methylbenzylamine (**15**) (0.64 mL, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at room temperature. When the collection was finished, methyl cyanoacetate (0.53 mL, 6 mmol) was added and the solution was concentrated under the reduced pressure. The residue was loaded on silica (1 g) and purified (eluent: hexane/EA from 98:2 to 80:20 over 20 column volumes) to give 2 diastereomers of **16** as colorless oils. Diastereomer A: 0.29 g (27%); R_f = 0.6 (hexane/ethyl acetate 4:1); ^1H NMR (400 MHz, CDCl_3): 1.99 (s, 3H), 3.52 (s, 3H), 7.35 (br.s., 5H); ^{13}C NMR (100 MHz, CDCl_3): 22.8, 53.6, 56.4, 70.1, 114.4, 126.3, 128.4, 129.2, 134.2, 161.9; HRMS (EI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{11}\text{NNaO}_3$ 240.0637, found 240.0631. Diastereomer B: 0.49 g (45%); R_f = 0.4 (hexane/ethyl acetate 4:1); ^1H NMR (400 MHz, CDCl_3): 1.83 (s, 3H), 3.94 (s, 3H), 7.41–7.46 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): 18.0, 54.2, 57.0, 70.1, 113.9, 126.0, 128.8, 129.6, 135.6, 162.8; HRMS (EI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{11}\text{NNaO}_3$ 240.0637, found 240.0635.

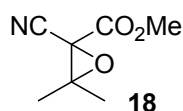


Methyl 2-cyano-1-oxaspiro[2.5]octane-2-carboxylate (14). TPP (7 mg) was added to a solution of cyclohexylamine (**13**) (0.57 mL, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at -60°C. When the collection was finished, methyl cyanoacetate (0.53 mL, 6 mmol) was added and

the solution was concentrated under the reduced pressure. The residue was loaded on silica (1 g) and purified (eluent: hexane/EA from 98:2 to 80:20 over 20 column volumes) to give epoxide **14** (0.68 g, 69%) as a colorless oil. $R_f = 0.5$ (hexane/ethyl acetate 4:1); ^1H NMR (400 MHz, CDCl_3): 1.47–1.89 (m, 10H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): 24.8, 24.8, 24.8, 28.5, 32.6, 54.0, 55.3, 71.9, 114.5, 163.1; HRMS (EI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{NNaO}_3$ 218.0793, found 218.0796.

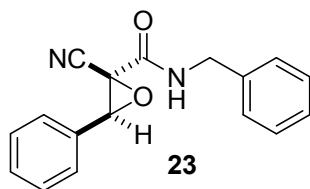


(2R,3S)-Methyl 2-cyano-3-methyloxirane-2-carboxylate (21). TPP (7 mg) was added to a solution of diethylamine (**20**) (0.52 mL, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at room temperature. When the collection was finished, methyl cyanoacetate (0.53 mL, 6 mmol) was added and the solution was concentrated under the reduced pressure. The residue was loaded on silica (1 g) and purified (eluent: hexane/EA from 98:2 to 80:20 over 20 column volumes) to give epoxide **21** (0.54 g, 76%) as a colorless oil. $R_f = 0.5$ (hexane/ethyl acetate 4:1); ^1H NMR (400 MHz, CDCl_3): 1.63 (d, $J = 5.2$ Hz, 3H), 3.59 (ddd, $J = 5.2, 5.2, 5.2$ Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): 15.0, 50.7, 54.2, 60.9, 113.6, 163.8; HRMS (EI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_6\text{H}_7\text{NNaO}_3$ 164.0324, found 164.0320.

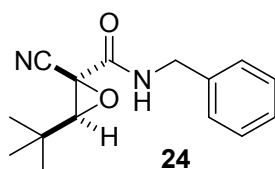


Methyl 2-cyano-3,3-dimethyloxirane-2-carboxylate (18). **From diisopropylamine (19):** TPP (7 mg) was added to a solution of diisopropylamine (**19**) (0.70 mL, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at room temperature. When the collection was finished, methyl cyanoacetate (0.53 mL, 6 mmol) was added and the solution was concentrated under the reduced pressure. The residue was loaded on silica (1 g) and purified (Eluent: hexane/EA from 98:2 to 80:20 over 20 column volumes) to give epoxide **18** (0.58 g, 75%) as a colorless oil. **From isopropylamine (17) at r.t.:** TPP (7 mg) was added to a solution of isopropylamine (**17**) (0.43 mL, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at r.t. When the collection was finished, methyl cyanoacetate (0.53 mL, 6 mmol) was added and the solution was concentrated under the reduced pressure. The residue was loaded on silica (1 g) and purified (eluent: hexane/EA from 98:2 to 80:20 over 20 column volumes) to give epoxide **18** (0.34 g, 43%) as a colorless oil. $R_f = 0.4$ (hexane/ethyl acetate 4:1); ^1H NMR (400 MHz, CDCl_3): 1.41 (s,

3H), 1.63 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): 18.2, 22.2, 54.0, 55.1, 67.3, 114.7, 163.1; HRMS (EI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_7\text{H}_9\text{NNaO}_3$ 178.0480, found 178.0480.



(2R,3S)-N-Benzyl-2-cyano-3-phenyloxirane-2-carboxamide (23). TPP (7 mg) was added to a solution of dibenzylamine (**22**) (0.96 mL, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at room temperature. When the collection was finished, methyl cyanoacetate (0.53 mL, 6 mmol) was added and the solution was concentrated under the reduced pressure. The residue was loaded on silica (1.5 g) and purified (eluent: hexane/EA from 95:5 to 60:40 over 20 column volumes) to give epoxide **23** (0.98 g, 71%) as white crystals. R_f = 0.7 (hexane/ethyl acetate 1:1); ^1H NMR (400 MHz, CDCl_3): 4.33 (s, 1H), 4.40–4.50 (m, 2H), 7.01 (br.s., 1H), 7.28–7.43 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3): 43.7, 55.5, 64.6, 113.4, 126.6, 127.9, 128.7, 128.8, 129.7, 130.3, 136.7, 161.5; HRMS (EI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{NaO}_2$ 301.0953, found 301.0949.

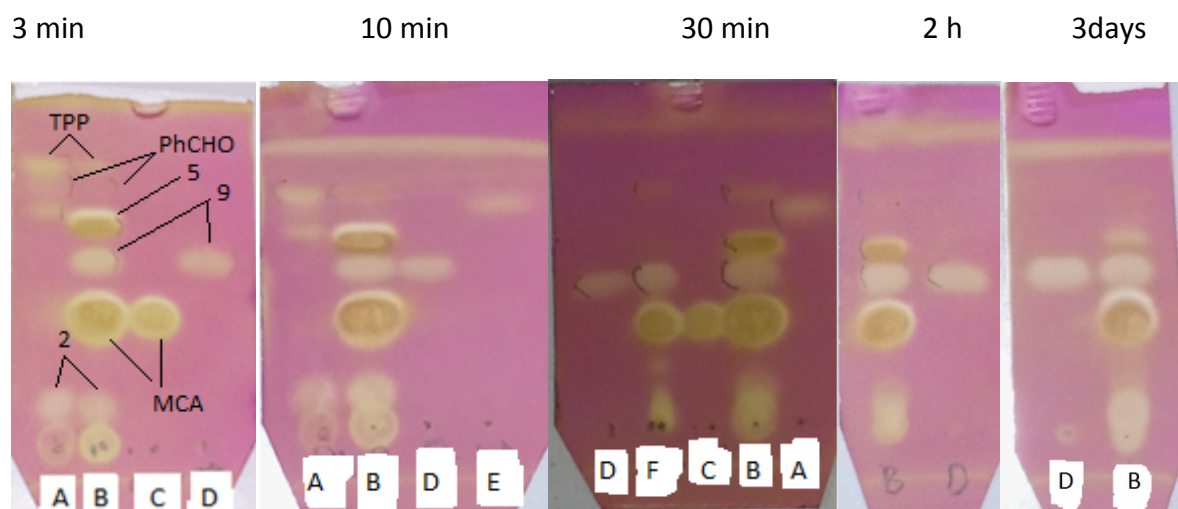


(2R,3S)-N-Benzyl-3-(tert-butyl)-2-cyano-2-oxirane-2-carboxamide (24). TPP (7 mg) was added to a solution of neopentylamine (**7**) (0.59 mL, 5 mmol) in 50 mL THF at room temperature. The resulting solution was mixed with oxygen gas and pumped through the photoreactor at -60°C . When the collection was finished, methyl cyanoacetate (0.53 mL, 6 mmol) was added and the solution was concentrated under the reduced pressure. Benzylamine (**1**) (0.55 mL, 5 mmol) was then added and concentrated under reduced pressure for 10 minutes. The residue was loaded on silica (1 g) and purified (eluent: hexane/EA from 98:2 to 80:20 over 20 column volumes) to give epoxide **24** (0.81 g, 63%) as a colorless oil. R_f = 0.4 (hexane/ethyl acetate 4:1); ^1H NMR (400 MHz, CDCl_3): 1.15 (s, 9H), 3.01 (s, 1H), 4.41 (ddd, J = 5.9, 14.6, 14.6 Hz, 1H), 4.45 (ddd, J = 5.9, 14.6, 14.6 Hz, 1H), 6.58 (br.s., 1H), 7.25–7.38 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): 26.2, 31.9, 43.8, 50.4, 72.4, 114.3, 128.1, 128.1, 129.0, 136.7, 162.7; HRMS (EI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{NaO}_2$ 281.1266, found 281.1274.

TLC studies

The solution after photooxidation of benzylamine (**1**) at $-60\text{ }^{\circ}\text{C}$ was treated with methyl cyanoacetate. The figure below presents reaction monitoring by TLC. As one could see, product (cyanoepoxide **9**) could be detected even after 3 min. Knoevenagel product (alkene **5**) could be observed in all TLCs, however its relative intensity after 3 days decreases. However, when a sample (2 mL) from the reaction flask after 30 min was evaporated for 5 min no alkene **5** was observed. This fact suggests that the reaction is much faster when concentrated under reduced pressure.

Hexane/EtOAc 3:1. Visualization by KMnO_4 .



Legend:

- Flask with a solution after photooxidation. TPP ($R_f = 0.81$) is nicely visible on the top of TLC. Directly under TPP, benzaldehyde ($R_f = 0.73$) is slightly detectable in KMnO_4 (high intensity spot in UV254). Near the baseline imine **2** (it's trimer, $R_f = 0.13$).
- Flask where the solution after photooxidation (A) was treated with methyl cyanoacetate (spot C). TPP and benzaldehyde are on the top of the plate. New spot ($R_f = 0.63$) of alkene **5** (Knoevenagel product) appeared (high intense in UV, easy to oxidize by KMnO_4). Another new spot ($R_f = 0.55$) of epoxide **9** appeared (very slow oxidation by KMnO_4).
- Methyl cyanoacetate (MCA, $R_f = 0.36$). UV not active. Very easy and intensively oxidized by KMnO_4 .
- Analytical sample of cyanoepoxides **9**.
- Commercially available benzaldehyde.
- 2 mL of solution B was taken and evaporated in a usual way. The residue was redissolved in THF.

