

Supporting Information

Aluminum(III) Salen Complexes as Active Photoredox Catalysts

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Table of contents

General methods and materials	2
Screening experiments	3
Synthesis of catalyst 9	4
Synthesis of aldehyde 11	4
General procedure for enantioselective photoalkylation of aldehydes	5
Characterization data of compounds 10aa-110ae	5
Synthesis of compound 13	7
Photochemical investigations	9
References	. 10
Copies of NMR spectra	11
HPLC traces	27

General methods and materials

¹H-NMR spectra were recorded on Varian Mercury 400 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (CDCl₃: δ = 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = duplet, t = triplet, q = quartet, dd = double duplet, dt = double triplet, bs = broad signal, m = multiplet), coupling constants (Hz). ¹³C-NMR spectra were recorded on Varian MR400 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (CDCl₃: δ = 77.0 ppm). GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. LC-electrospray ionization mass spectra (ESI-MS) were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Enantiomeric excess was determined by using Agilent Technologies 1200 HPLC instrument equipped with a variable wave-length UV detector (reference 420 nm), using Daicel Chiralpak[®] columns (0.46 cm I.D. x 25 cm) and HPLC grade *i*-propanol and *n*-hexane as eluting solvents. Chromatographic purification was done with 240-400 mesh silica gel. All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques.

Anhydrous solvents were supplied by Aldrich in Sureseal® bottles and were used without further purification. All the reagents were purchased from Aldrich and used without further purification unless specified.

Compounds 1, 2, S1, S2, S3: commercially available

Compounds $3^{[1]} 4^{[2]} 5^{[2]} 6^{[3]} 7d^{[4]} 7e^{[5]} 8d, e^{[6]} (2R, 5S) - 2-t-butyl-3, 5-dimethylimidazolin-4-one monohydrochloride, [7] S4, [8] S5, [9] S6, [10] S7, [11] and S8 [12] were prepared according to reported procedures.$

Screening experiments

Table S1. Screening of Salen and Salophen complexes in photocatalytic stereoselective alkylation of aldehyde 7a with 8a.



Entry ^[a]	Metal complex	Conversion (%) ^[b]	ee (%) ^[c]
1	1	37	
2	2	99 (83) ^[d]	89
3	3	64	88
4	4	50	89
5	5	68	89
6	6	72	88
7	-	12	
8	S1	0	
9	S2	0	
10	S3	0	
11	S4	25	89
12	S5	0	
13	S6	61	89
14	S7	37	88
15	S8	50	89

[a] Reaction was performed on 0.2 mmol of **8a** in DMF (1 mL). [b] Conversion determined by ¹H NMR analysis of reaction crude using internal standard method. [c] Enantiomeric excesses were determined by HPLC on chiral stationary phase. [d] Yield determined after chromatographic purification.

Table S2. Screening of Salen and Salophen complexes in photocatalytic stereoselective alkylation of aldehyde 7a with 8a.

0 H 7a, 2 equ	CO2Et Bn + Br CO2Et uiv 8a	N TfO [⊖] ⊕tBu H H 9, 14 mol% hv, CFL (23 W) Al(III) complex, 5 mol% 2,6-lutidine, 2 equiv DMF, rt, 18 h		₂Et CO₂Et Iaa	
Entry ^[a]	Al(III) complex	Al(III) complex (mol%)	9 (mol%)	Conversion (%) ^[b]	ee (%) ^[c]
1	2	5	14	99 (83) ^[d]	89
2	2	5	28	99 (80) ^[d]	89
3	2	3.5	14	95 (76) ^[d]	89
4	ent -2	5	14	96 (80) ^[d]	89
5	2	5	20 ^[e]	89 (72) ^[d]	0
6	3	5	14	86	88
7	3	3.5	14	64	88
8	5	5	14	68	89
9	5	3.5	14	54	88

[a] Reaction was performed on 0.2 mmol of **8a** in DMF (1 mL). [b] Conversion determined by ¹H NMR analysis of reaction crude using internal standard method. [c] Enantiomeric excesses were determined by HPLC on chiral stationary phase. [d] Yield determined after chromatographic purification. [e] Reaction performed using morpholine as organocatalyst.

Synthesis of catalyst 9

MacMillan catalyst (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolin-4-one monohydrochloride^[7] (321 mg, 1.30 mmol) was dissolved in NaHCO₃ aq. sat. solution (4 mL) inside a separator funnel and the aqueous layer was extracted with CHCl₃ (5 x 5 mL). The collected organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The resulting oil was dissolved in dry Et₂O (5 mL) and cooled to 0°C. Triflic acid (1.9 mmol, 167 μ L) was added dropwise under stirring and a white solid precipitated. After 10 min the solution was filtered on a Gooch septum and the solid was washed with Et₂O (2.5 mL) and pentane (10 mL), recovered and dried under vacuum to furnish **9** (358 mg, 1.12 mmol, 86% yield) as white solid.

Synthesis of aldehyde 11



The reaction was performed follow the procedure reported in literature.^[13] To a solution of alcohol **11** (1.83 mL, 14.7 mmol) in anhydrous acetonitrile (15 mL), copper salt (0.05 equiv., 274 mg, 0.73 mmol), 2,2'-bipyridine (0.05 equiv., 115 mg, 0.73 mmol), TEMPO (0.05 equiv., 115 mg, 0.73 mmol) and *N*-methylimidazole (0.1 equiv., 117 μ L, 1.47 mmol) were added under N₂ atmosphere. The reaction was stirred under O₂ atmosphere for 22 h and HCl (1M, 5 mL) was added. The mixture was extracted with *n*-hexane (3 x 15 mL). The collected organic phases were washed with brine (15 mL) and dried over Na₂SO₄

anhydrous. The solvent was evaporated at atmospheric pressure under gently stirring and heating. The product was obtained as liquid in 64% yield and with 77% of purity (in mixture with hexane). The product was used in the next step without further purification.

¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 9.76 (t, *J* = 1.9 Hz, 1H), 2.54 – 2.19 (m, 2H), 1.63 – 1.46 (m, 3H), 0.90 (d, *J* = 6.5 Hz, 6H); ¹³C-NMR (100 MHz, CDCl₃, 25°C): δ = 202.8, 41.9, 31.5, 27.5, 22.1 (2C).

General procedure for enantioselective photoalkylation of aldehydes

In a Schlenk tube with rotaflo stopcock under argon atmosphere at r.t., **2** (0.05 equiv., 6 mg, 0.01 mmol) and the MacMillan catalyst **9** (0.14 equiv., 9 mg, 0.028 mmol) were dissolved in 1 mL DMF. Aldehydes **7a-e** (2 equiv, 0.4 mmol), bromo derivatives **8a-e** (1 equiv, 0.2 mmol) and 2,6-lutidine (2 equiv., 48 µL, 0.4 mmol) were then added.

The reaction mixture was carefully degassed via freeze-pump thaw (three times), and the vessel refilled with argon. The Schlelk tube was stirred and irradiated with a 23 W CFL bulb positioned approximately at 10 cm distance from the reaction vessel. After 18 h of irradiation, aq. HCl 1M (2 mL) was added and the mixture was extracted with AcOEt (4 x 5 mL). The collected organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. Products were purified by column flash chromatography on SiO₂.

Racemic compounds were synthesized according to general procedure using morpholine (20 mol%) instead of 9.

General procedure for determination of enantiomeric excesses of compounds 6-9.

Products **10ba**, **10ea** and **10fa** were transformed in their corresponding diastereomeric acetals according to the literature protocol^[14] in order to determine their enantiomeric excess.

To a solution of aldehyde (0.05 mmol) in DCM (1.0 mL), (2R,4R)-(-)- (for **10fa**) and (2S,4S)-(+)-pentanediol (for **10ba** and **10ea**) (>99% ee, 12.5 mg, 0.12mmol) and *p*-toluenesulfonic acid monohydrate (1.9 mg, 0.01 mmol) were added. The solution was stirred at rt until complete conversion was observed by TLC analysis. The mixture was concentrated under reduced pressure. Enantiomeric excesses were calculated from diastereomeric ratios of the resulting acetals, determined either by ¹H NMR analysis.

Characterization data of compounds 10aa-110ae



10aa: the title compound was isolated by flash column chromatography (SiO₂, cyclohexane/EtOAc 95/5) as
CO₂Et colourless oil (49 mg, 0.17 mmol, 83% yield, 89% ee before column separation and 83% ee after column purification). ee was determined by chiral HPLC analysis using Daicel Chiralpak[®]IC column: hexane/*i*-PrOH

90:10, flow rate 1.00 mL/min, 30°C, λ = 210 nm: τ_{major} = 18.9 min., τ_{minor} = 14.7 min.; ¹H NMR and ¹³C NMR were according to those reported in literature.^[14]

10ab: The title compound was isolated by flash column chromatography (SiO₂, cyclohexane/EtOAc 95/5)as colourless oil (45 mg, 0.17 mmol, 85% yield, 89% ee before column separation and 79% ee after column purification). ee was determined by chiral HPLC analysis using Daicel Chiralpak[®]IC column: hexane/*i*-PrOH

90:10, flow rate 1.00 mL/min, 30°C, λ = 210 nm: τ_{major} = 23.56 min., τ_{minor} = 18.69 min.; ¹H NMR and ¹³C NMR were according to those reported in literature.^[15]



10ba: The title compound was isolated by flash column chromatography(SiO2, cyclohexane/EtOAc 95/5) as colourless oil (41.4 mg, 0.1447 mmol, 72% yield, 89% ee). Ee was determined after derivatization of 29 mg of the title compound to its corresponding diastereomeric acetal following general procedure. Ee was

determined by integration of the two ¹H NMR (400 MHz, CDCl₃, 25°C) signals at 3.62 ppm (major, doublet) and 3.68 ppm (minor, doublet) corresponding to the two diastereomeric acetals.¹H NMR and ¹³C NMR were according to those reported in literature.^[14]



10ca: The title compound was isolated by flash column chromatography (SiO₂, cyclohexane/EtOAc 95/5) as colourless oil (42 mg, 0.15 mmol, 72% yield, 89% ee). ee was determined by chiral HPLC analysis using Daicel Chiralpak[®]IC column: hexane/*i*-PrOH 90:10, flow rate 1.00 mL/min, 30°C, λ = 210 nm: τ_{major} = 11.78 min., τ_{minor} = 13.03 min.; ¹H NMR and ¹³C NMR were according to those reported in literature.^[14]



10da: The title compound was isolated by flash column chromatography (SiO₂, cyclohexane/EtOAc from 98/2 to 90/10) as colourless oil (29 mg, 0.102 mmol, 50% yield, 91% ee after column purification). ee was determined by chiral HPLC analysis using Daicel Chiralpak[®]IA column: hexane/*i*-PrOH 97:3, flow rate 1.00 mL/min, 30°C, λ = 210 nm: τ_{major} = 8.304 min., τ_{minor} = 9.938 min.. ¹H NMR and ¹³C NMR were according to

those reported in literature.[14]



10ea: The title compound was isolated by flash column chromatography (SiO₂, cyclohexane/EtOAc, 8/2) as colourless oil (35 mg, 0.09 mmol, 45% yield, 88% ee before column separation and 83% after column purification). ee was determined after derivatization of 19 mg of the title compound to its corresponding diastereomeric acetal following general procedure. Ee was determined by integration of the two ¹H NMR

(400 MHz, CDCl₃, 25°C) signals at 5.10 ppm (*major*, doublet) and 5.05 ppm (*minor*, doublet) corresponding to the two diastereomeric acetals.¹H NMR was according to those reported in literature.^[14]



10ac: The title compound was isolated by flash column chromatography(SiO₂, cyclohexane/EtOAc 97/3) as a colourless oil (20 mg, 0.08 mmol, 40% yield, 93% ee before column purification). Ee was determined by chiral HPLC analysis using Daicel Chiralpak[®]IC column, hexane/*i*-PrOH 90:10, flow rate 1.00 mL/min, 30°C,

λ = 210 nm: *τ_{major}*= 17.8 min., *τ_{minor}* = 14.9 min.; ¹H NMR and ¹³C NMR were according to those reported in literature.^[15]



10ad: The title compound was isolated by flash column chromatography (SiO₂, cyclohexane/EtOAC 95/5) as a white solid (0.112 mmol, 56% yield, 92% ee before column, 83% ee after column purification). Ee was determined by chiral HPLC analysis using Daicel Chiralpak[®]IC column, hexane/*i*-

PrOH 90:10, flow rate 1.00 mL/min, 30°C, λ = 210 nm: τ_{major} = 14.7 min., τ_{minor} = 13.7 min.; ¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 9.87 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.17 (d, *J* = 7.4 Hz, 2H), 3.42 – 3.31 (m, 2H), 3.15 (dd, *J* = 13.9, 5.9 Hz, 1H), 2.97 – 2.89 (m, 1H), 2.80 (dd, *J* = 13.9, 8.1 Hz, 1H); ¹³C-NMR (100 MHz, CDCl₃, 25°C): δ = 202.7, 196.8, 137.9, 135.1, 131.9 (2C), 129.5 (2C), 129.0 (2C), 128.8 (2C), 128.5, 126.8, 48.4, 37.0, 34.6; [α]_D (c = 0.2, CH₂Cl₂): + 14.3.



10ae: The title compound was isolated by flash column chromatography(SiO₂, cyclohexane/EtOAc 97/3) as a yellowish oil (37 mg, 0.13 mmol, 64% yield, 92% ee). Ee was determined by chiral HPLC analysis using Daicel Chiralpak[®]IC column, hexane/*i*-PrOH 95:5, flow rate 1.00 mL/min, 30°C, λ = 214

nm: Tmajor= 19.9 min., Tminor = 18.2 min.; ¹H NMR and ¹³C NMR were according to those reported in literature.^[15]

10fa: The title compound was isolated by flash column chromatography(SiO2, cyclohexane/EtOAc 95/5) as $H \xrightarrow{CO_2Et}$ colourless oil (44 mg, 0.17 mmol, 86% yield, 94% ee). Ee was determined after derivatization of 19 mg of the title compound to its corresponding diastereomeric acetal following general procedure. Ee was determined by integration of the two ¹H NMR (400 MHz, CDCl₃, 25°C) signals at 3.45 ppm (major, doublet) and 3.53 ppm (minor, doublet) corresponding to the two diastereomeric acetals: ¹H-NMR (400 MHz, CDCl₃, 25°C): $\overline{\delta}$ = 9.78 (s, 1H), 4.27 – 4.14 (m, 4H), 3.69 (d, *J* = 7.9 Hz, 1H), 3.09 (q, *J* = 7.8 Hz, 1H), 1.67 (ddd, *J* = 14.1, 9.9, 5.9 Hz, 2H), 1.30 – 1.21 (m, 7H), 0.94 (d, *J* = 6.2 Hz, 3H), 0.91 (d, *J* = 6.2 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃, 25°C): $\overline{\delta}$ = 201.8, 168.0, 167.9, 61.9, 61.8, 52.7, 48.3, 36.5, 22.1, 14.2, 14.1, 14.0 (2C); [α]_D (c = 0.2, CH₂Cl₂): - 48.5.

Synthesis of compound 13





12: To a solution of crude aldehyde **10fa** (103 mg, 0.4 mmol) from photochemical alkylation reaction in dry dichloromethane (3 mL), benzylamine (1.2 equiv., 52 μ L, 0.48 mmol), pyrrolidine (0.02 equiv., 0.08 mmol, 1 μ L approx.) and 4 Å molecular sieves (50 mg) were added.^[16] After completing disappear of aldehyde (by ¹H-NMR analysis), anhydrous methanol (5 mL) and NaBH₄ (2 equiv., 30 mg, 0.4 mmol) were added at 0°C.

The reaction mixture was stirred at room temperature for 3 hours. After that AcOEt (15 mL) and water (10 mL) were added and the two layers were separated. Water phase was extracted with AcOEt (2 x 15 mL) and the combined organic layers were washed with brine (10 mL), dried over Na₂SO₄, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (SiO₂, cyclohexane to cyclohexane/ethyl acetate, 8/2) to afford **12** (71%, 86 mg, 0.28 mmol) as mixture of diastereoisomers (90:10 by ¹H-NMR).

¹H-NMR (400 MHz, CDCl₃, 25°C) major diastereoisomer: δ = 7.36 – 7.26 (m, 3H), 7.24 – 7.19 (m, 2H), 4.44 (s, 2H), 4.24 (q, *J* = 7.2, 6.8 Hz, 2H), 3.40 (dd, *J* = 9.0, 7.9 Hz, 1H), 3.13 (d, *J* = 7.9 Hz, 1H), 2.87 – 2.71 (m, 2H), 1.54 – 1.42 (m, 1H), 1.42 – 1.33 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.27 – 1.19 (m, 1H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃, 25°C) major diastereoisomer: δ = 170.2, 169.8, 135.9, 128.7 (2C), 128.1 (2C), 127.7, 61.5, 55.5, 51.1, 46.9, 43.3, 34.4, 25.8, 22.5, 22.4, 14.1.; GC-MS: rt 18.64; *m/z* = 303 (M⁺⁻, 018), 246 ([M-*i*-Bu]⁺⁻, 38), 200 (30), 172 (26) 91 (100); ESI-MS *m/z*: 304.3 [M+H]⁺.

Bn o 13: To a solution of compound 12 (80 mg, 0.26 mmol) in *t*-BuOH (2 mL), KOH (1 M in water, 1 mL) was slowly added. The reaction mixture was vigorous stirred for 24 hours and the solvent was evaporated. Water (5 mL) was added and the mixture was extracted with diethyl ether (5 mL). Aqueous phase was washed with diethyl ether (5 mL). HCl 1M was slowly added to aqueous phase until pH = 1 and the mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were washed with brine (10 mL), dried over Na₂SO₄, and the solvent was removed under reduced pressure.

Crude acid was dissolvent in toluene (5 mL) and refluxed for 10 hours. The solvent was evaporated, and the residue was purified by flash column chromatography (SiO₂, cyclohexane to cyclohexane/ethyl acetate, 9/1) to afford **13** (83%, 49 mg, 0.21 mmol)

¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 7.34 – 7.25 (m, 3H), 7.23 – 7.18 (m, 2H), 4.45 (d, *J* = 14.7 Hz, 1H), 4.39 (d, *J* = 14.7 Hz, 1H), 3.32 (t, *J* = 9.3, 8.1 Hz, 1H), 2.85 (dd, *J* = 9.5, 6.9 Hz, 1H), 2.56 (dd, *J* = 16.4, 9.9 Hz, 1H), 2.45 – 2.29 (m, 1H), 2.10 (dd, *J* = 16.4, 8.0 Hz, 1H), 1.56 - 1.45 (m, 1H), 1.36 – 1.19 (m, 2H), 0.85 (d, *J* = 6.3 Hz, 3H). 0.84 (d, *J* = 6.3 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃, 25°C): δ = 174.8, 136.5, 128.7 (2C), 128.1 (2C), 127.5, 77.3, 76.7, 52.7, 46.6, 44.0, 38.0, 29.8, 26.1, 22.6, 22.5; ESI-MS *m/z*: 232.1 [M+H]⁺, 463.1 [2M+H]⁺; [α]_D (c = 0.2, CH₂Cl₂): + 3.6.

Photochemical investigations



Figure S1. Emission profile of the 23W Compact Fluorescent lamp used to irradiate the solutions.

Figure S2. Reaction mixture in DMF, contains [Al(Salen)Cl] **2** 1.2×10⁻³ M, 2,6-lutidine 0.4 M, diethyl bromomalonate **8a** 0.2 M, 3-phenylpropanal **7a** 0.4 M and imidazolidinone catalyst **9** 0.04 M, irradiated for 0 min (light blue solid line), 30 min, 60 min, 120 min, 240 min and 360 min (black solid line); transmittance spectrum cut-of filter used during the irradiation (orange dotted line) Optical pathlength 0.1 cm.



Figure S3. Emission intensity decays of [Al(Salen)Cl] 2 in DMF solution in presence of 2,6-lutidine 0.4 M, diethyl bromomalonate 8a 0.2 M, 3-phenylpropanal 7a 0.4 M and imidazolidinone catalyst 9 0.04 M, before (blue dots) and after 6h of irradiation (orange dots) upon excitation at 340 nm.



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Copies of NMR spectra



















Racemic



Active













Racemic









Racemic

HPLC traces

