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Supporting Information

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1. General Experimental Information

Unless otherwise specified, reagents were obtained from commercial suppliers and used without further purification. Solvents were reagent grade and used without purification unless otherwise noted. All glasswares were oven dried at 120 °C for hours and cooled down to room temperature. Reticulated vitreous carbon (RVC, 100 PPI, 10 mm x 10 mm x 2 mm) were used as anode or cathode. Analytical thin-layer chromatography (TLC) was conducted with TLC silica gel GF254 under UV irradiation. Flash column chromatography was performed using silica gel 300 and columns were packed according to the dry or wet method. Nuclear Magnetic Resonance spectra were recorded on a Bruker Advance 400 (400 MHz) NMR spectrometer and ¹H NMR reported in units of parts per million (ppm) relative to tetramethyl silane (δ 0 ppm) or CDCl₃ (δ 7.26 ppm). Multiplicities are given as: bs (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublets of doublet), dt (doublets of triplet) or m (multiplet). ¹³C NMR spectra were recorded on a Bruker Advance 400 (101MHz) NMR spectrometer and reported in ppm relative to $CDCl_3$ (δ 77.0 ppm). Coupling constants were reported as a J value in Hz. GC analyses were performed using a Varian star GC spectrometer. CV determination was performed on CHI 760E (CH Instruments, Ins) with glassy carbon as working electrode, Ag/AgNO3 reference electrode and a platinum wire counter electrode. Ag/AgNO₃ reference electrodes were stored in an acetonitrile solution with 0.01 M AgNO₃ and 0.1 M LiClO₄ before use. The instrument for bulk electrolysis is dual display potentiostat (DJS-292B) (Shanghai xinrui instruments co., LTD), RVC-reticulated vitreous carbon.

2. General Procedures for Mncl2-catalyzed oxychlorination



General procedure for external oxidant-free electrooxidative the difunctionalization for the synthesis of 2-chloroacetophenone: To an oven-dried undivided glass vial (20 mL), MnCl₂ (2.5 mg, 0.02 mmol. 10 mol %), MgCl₂·6H₂O (121.9 mg, 0.6 mmol, 3.0 equiv.), LiClO₄ (63.8 mg, 0.6 mmol, 3.0 equiv.) was added. The bottle was equipped with a rubber septum and RVC (100 PPI, 10 mm x 10 mm x 2 mm) as the anode and cathode. The cell was sealed and flushed with oxygen for 15 minutes, followed by the sequential addition of olefin substrates (23 μ l, 0.20 mmol, 1.0 equiv.), acetone (5.9 mL) and DCM (0.1 mL) via syringe. Then the bulk electrolysis was started at a constant current of 5 mA at 40 °C for 12 h. When the reaction completed as indicted by TLC, the pure product (white solid 28.6 mg, 93% Yield.) was obtained by flash column chromatography on silica gel (Petroleum ether : ethyl acetate = 20:1). Regarding reticulated vitreous carbon (RVC, 100 PPI, 10 mm x 10 mm x 2 mm) as the electrode, the sheet of RVC was connected by the graphite rod with a sharpened head and the reaction was run for 12 h unless otherwise stated.

3. Optimization of the reaction conditions.

1. Table S1. Solvent screening

LiC	(+)RVC-RVC(-), I = 5 mA MnCl ₂ (10 mol %) <u>MgCl₂ 6H₂O (3 equiv.)</u> CIO ₄ (3 equiv.), <mark>O</mark> ₂ , 12 h, 40 °C	-	
Entry	Solvent	Yield	
1	MeCN	42%	
2	Acetone	65%	
3	DCM	0%	
4	DMF	Trace	
5	DMA	18%	
6 ^a	Acetone/DCM	93%	

Reaction conditions: MnCl₂ (10 mol %), MgCl₂.H₂O (3 equiv.), electrolyte (3 equiv.), solvent (6 mL), 12h, 40 °C, O₂ bubbling. Acetone-DCM (5.9 mL-0.1 mL).

2. Table S2. Catalyst screening

(+ N LiClO₄ Ace)RVC-RVC(-), I = 5 mA $MgCl_2 \cdot 6H_2O$ (3 equiv.) (3 equiv.), O ₂ , 12 h, 40 °C etone-DCM (5.9-0.1 mL)		CI
Entry	Catalyst	Yield	
1	$MnCl_2(10 mol\%)$	93%	
2	FeCl ₂	40%	
3	Crcl ₃ ·6H ₂ O	18%.	
4	Nicl ₃ ·6H ₂ O	40%	
5	$Cucl_2 \cdot 2H_2O$	8%	
6	None	0%	

Reaction conditions: Catalyst (10 mol %), MgCl₂.H₂O (3 equiv.), electrolyte (3 equiv.), solvent (6 mL), 12h, 40 °C, O₂ bubbling.

3. Table S3. Reaction time screening

_	CI		
Entry	Reaction time	Yield	
1	3h	23%	
2	6h	67%	
3	8h	66%.	
4	12h	93%	

Reaction conditions: Catalyst (10 mol %), MgCl₂.H₂O (3 equiv.), electrolyte (3 equiv.), solvent (6 mL), 40 °C, O₂ bubbling.

4. Table S4. Electrode material



Reaction conditions: MnCl₂ (10 mol %), MgCl₂.H₂O (3 equiv.), electrolyte (3 equiv.), Acetone-DCM (5.9 mL-0.1 mL), 12h, 40 °C, O₂ bubbling.

4. Typical procedure for the gram-scale synthesis of 2.



1 8 mmol

283% 1.03 g

To an oven-dried three-neck glass tube (100 mL), MnCl₂ (100.7 mg, 0.8 mmol, 10 mol %), MgCl₂·6H₂O (4.877 g, 24 mmol, 3.0 equiv.), LiClO₄ (2.553 g, 24 mmol, 3.0 equiv.) and a string magnetic bar was added. The tube was fitted with a rubber septum with RVC (100 PPI, 10 mm × 50 mm × 0.2 mm) as the anode and cathode. The cell was sealed and flushed with oxygen for 15 minutes, followed by the sequential addition of olefin substrate (920 μ L, 8.0 mmol, 1.0 equiv.), acetone (59 mL) and DCM (1.0 mL) via syringe. Then the mixture was electrolyzed at a constant current of 40 mA at 40 °C for 40 h. When the reaction completed as indicted by TLC,

the pure product (white solid 1.03 g, 83% yield) was obtained by flash column chromatography on silica gel (Petroleum ether : ethyl acetate = 20:1).

5. Cyclic voltammetry studies

Cyclic voltammetry (CV) experiments were conducted in a 25 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter, BASi), a Ag/AgNO₃ reference electrode, and a platinum wire counter electrode. Ag/AgNO₃ reference electrodes were stored in an acetonitrile solution with 0.01 M AgNO₃ and 0.1 M LiClO₄. And LiClO₄ (1.2 mM), MnCl₂ (0.12 mM), MgCl₂·6H₂O (0.12 mM), Styrene. (0.12 mM), O₂ (Bubbling) and their mixture in acetone / DCM (11.8 mL / 0.2 mL). Scan rate: 100 mV/s.





5. Characterization data of products



2-Chloro-1-phenylethanone (2)^[1] Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give white solid 28 mg, 93% Yield. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 4.72 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 191.0, 134.2, 134.0, 128.9, 128.5, 46.0.



2-Chloro-1-(p-tolyl)ethanone (3)^[1] Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give colorless crystals 31.6 mg, 95% Yield. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8Hz, 2H), 7.14 (d, *J* = 8Hz, 2H), 4.55 (s, 2H), 2.27 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 190.5, 144.9, 131.6, 129.4, 128.4, 46.9, 21.5



2-Chloro-1-(*m***-tolyl)ethanone (4)**^[1] Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give colorless crystals 23.3 mg, 69% Yield. ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.73 (m, 2H), 7.42 – 7.38 (m, 2H), 4.71 (s, 2H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃)

CDCl₃) δ 191.2, 138.8, 134.8, 134.3, 129.0, 128.8, 125.7, 46.0, 21.3.



2-Chloro-1-(o-tolyl)ethanone (5)^[1] Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give colorless oil 20.2 mg, 60% Yield. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 7.7 Hz, 1H), 7.22-7.18 (m, 1H), 7.08-7.04 (m, 2H), 4.44 (s, 2H), 2.31 (s, 3H).¹³C NMR (101 MHz, CDCl₃) δ 193.2, 138.3, 133.6, 131.4, 127.9, 125.0, 47.3, 20.4.



2-Chloro-1-(4-*tert***-butylphenyl)ethanone (6)**^[2] Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give syrup 37.9 mg, 90% Yield. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 4.69 (s, 2H), 1.35 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 190.7, 157.9, 131.6, 128.5, 125.8, 46.0, 35.2, 31.0.



2-Chloro-1-(4-methoxyphenyl)ethanone (7)^[2] Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give white solid, 26.1 mg, 71% Yield. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.66 (s, 2H), 3.88 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 189.6, 164.1, 131.0, 127.2, 114.1, 55.5, 45.7.



1-(4-Acetyloxyphenyl)-2-chloroethanone (8)^[2] Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give white solid 21 mg, 48% Yield. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 4.68 (s, 2H), 2.33 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 189.9, 168.7, 155.0, 131.7, 130.3, 122.2, 45.8, 21.1.

F CI

2-Chloro-1-(4-fluorophenyl)ethanone (9)^[1]: Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give white solid 23.5 mg, 68% Yield.¹H NMR (400 MHz, CDCl₃) δ 7.98-7.95 (m, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 4.66 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 189.6, 166.0 (d, *J*_{CF} = 257.6 Hz), 131.2 (d, *J*_{CF} = 9.1 Hz), 130.5 (d, *J*_{CF} = 3.0 Hz), 116.1 (d, *J*_{CF} = 22.2 Hz), 45.6.



2-Chloro-1-(3-fluorophenyl)ethanon (10)^[2]: Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give colorless oil 24 mg, 70% Yield. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 9.1 Hz, 1H), 7.49-7.44 (m, 1H), 7.32-7.28 (m, 1H), 4.68 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 190.0 (d, *J*_{CF} = 2.0 Hz), 162.8 (d, *J*_{CF} = 249.5 Hz), 136.2 (d, *J*_{CF} = 6.1 Hz), 130.7 (d, *J*_{CF} = 7.1 Hz), 124.3 (d, *J*_{CF} = 3.0 Hz), 121.1 (d, *J*_{CF} = 22.2 Hz), 115. 3 (d, *J*_{CF} = 22.2 Hz), 45.9 .



2-chloro-1-(4-chlorophenyl)ethanone (11)^[2]: Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO4 (3 equiv.), (+)RVC-RVC(-), 11h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give white solid 33 mg, 93% Yield. ¹H NMR (400MHz, CDCl₃) δ 7.90 (d, *J* = 8.0Hz, 2H), 7.48 (d, *J* = 8.4Hz, 2H), 4.66 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 189.9, 140.4, 132.4, 129.8, 129.1, 45.6.



2-chloro-1-(3-chlorophenyl)ethanone (12)^[3]: Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give red liquid 33.7 mg, 89% Yield. ¹H NMR (400 MHz, CDCl₃) δ 7.83 - 7.76 (m, 2H), 7.50 (d, *J* = 8 Hz, 1H), 7.40 - 7.37 (m, 1H), 4.67 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 189.7, 135.3, 134.8, 133.6, 130.0, 128.1, 126.3, 45.9.



2-chloro-1-(2-chlorophenyl)ethanone (13)^[4]: Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give white solid 14 mg, 37 % Yield. ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8 Hz, 1H), 7.46-7.45 (m, 2H), 7.39-7.36 (m, 1H), 4.70 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 194.2, 136.2, 132.8, 131.3, 130.6, 130.0, 127.2, 48.6.



1-(4-Bromophenyl)-2-chloroethanone (14)^[2]: Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give white solid 43 mg, 92 % Yield. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 4.65 (s, 2H).¹³C NMR (101 MHz, CDCl₃) δ 193.7, 135.0, 132.3, 130.1, 127.1, 45.6.



2-Chloro-1-(4-(trifluoromethyl)phenyl)ethanone(15)^[1]: Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂ 6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give white solid 34.6 mg, 78% Yield.¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 4.71 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 190.3, 136.9, 135.2 (q, *J*_{CF} = 32.3 Hz), 129.0, 126.0 (q, *J*_{CF} = 4.04 Hz), 123.4 (q, *J*_{CF} = 272.7 Hz), 45.7.



2-Chloro-4'-cyanoacetophenonev (16)^[5]: Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give white solid 26.3 mg, 77 % Yield. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 4.69 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 190.1, 137.1, 132.7, 129.1, 126.7, 117.3, 45.4.



2-Chloro-1-phenylpropan-1-one (17)^[1]: Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give colorless oil 32 mg, 92% Yield. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8 Hz, 2H), 7. 39 (t, *J* = 8 Hz, 1H), 7. 30-7.26 (m, 2H), 5.16 (q, *J* = 8 Hz, 1H), 1.56 (d, *J* = 8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 192.9, 134.0, 133.5, 128.3, 128.2, 52.4, 19.3.



2-Chloro-1,2-diphenylethanone (18)^[1]: Olefins (1 equiv, 0.2 mmol), MnCl₂ (10 mol%), MgCl₂·6H₂O (3 equiv.), LiClO₄ (3 equiv.), (+)RVC-RVC(-), 12h, I = 5 mA, O₂ balloon, acetone-DCM (5.9-0.1 mL), and purified using silica gel chromatography to give colorless oil 40 mg, 87% Yield. ¹H NMR (400 MHz, CDCl₃) δ 7.97-7.95 (m, 2H), 7.55 (t, *J* = 8Hz, 1H),7.49 – 7.34 (m, 7H), 6.32 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 191.4, 135.8, 134.2, 133.6, 129.1, 129.04, 129.01, 128.7, 128.4, 62.2

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NMR spectra of the products:









































































