Supporting Information:

Selective water-based oxychlorination of phenol with hydrogen

peroxide catalyzed by manganous sulfate

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(A) General Remarks

All materials and reagents were commercial received from Sinopharm Chemical Reagent Co. Ltd. and used without treatment.

Gas chromatography analyses were carried out on a Varian 450-GC with HP-5 column (30m×0.25mm, 1.0um) and a Varian CP-8400 autosampler. Analyses of gas chromatography-mass spectrometer and high performance liquid chromatography Liquid chromatography were performed on an Agilent 7890A-5975C with HP-5 column (15m×0.25mm, 1.0um) and a Waters 1525 with 2489 UV-Vis detector and 2707 autosampler using Eclipe Plus C18 column (250mm×4.6mm, 5.0um),

respectively. ¹H and ¹³C-NMR were recorded on a Bruker AVANCE-III 600 MHz in CDCl₃ (chemical shifts in δ with TMS as internal standard). Column chromatography was carried out using silica gel 200-300 mesh.

Table 1S.	Results f	or oxychlor	ination of	phenol d	lerivatives	calculate	۶d
from GC	data.						

Run	Substrata	Droduct	Time	Conversion ^a	Yield ^b
	Substrate	Product	(h)	(%)	(%)
1 ^c	р- сі		4	100	96
2 ^c	0- CI	1b CI	4	100	94
3	За	3b CI	3	100	75
4	4a	4b	3	100	81
5	5а	5b CI	3	100	86
6 ^d	6a	6b CI	3	100	82



Reaction conditions: substrate: 21.3 mmol, catalyst: 1 mol%, HCI: 44.7 mmol, H_2O_2 (30% aq. solution): 6.08 ml, 58.8 mmol, H_2O : 9.8 ml, 80 °C. a: conversion (%)=[the converted substrate (mol)/initial substrate (mol)]×100; b: yield (%)=[target product (mol)/initial substrate (mol)]×100; c: HCI: 23.4 mmol; d: t-butylammonium bromide: 0.1 mmol.

(B) ¹H NMR and ¹³C NMR spectra of products





















