Eur. J. Org. Chem. **2005** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2005 · ISSN 1434–193X

SUPPORTING INFORMATION

Title: Highly Efficient Catalytic Nitration of Phenolic Compounds by Nitric Acid with a Recoverable and Reusable Zr or Hf Oxychloride Complex and KSF
Author(s): Min Shi,* Shi-Cong Cui, Wan-Po Yin
Ref. No.: O040921

General Remarks.

MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J-values are in Hz. All of the solid compounds reported in this paper gave satisfactory CHN microannalyses with a Carlo-Erba 1106 analyzer. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA^{+} mass spectrometer. Organic solvents were dried by standard methods when necessary. Montmorillonite KSF (C.A.S.: 1318-93-0) was purchased from Acros Co. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. The orientation of nitration was determined by NMR analysis. Flash column chromatography was carried out using 200-300 mesh silica gel.

Preparation of Zirconium and Hafnium Oxychloride Complex.

$ZrCl_4$ or $HfCl_4$ (500 mg) was hydrolyzed with distilled water (2.0 mL) in a glass vessel. The excessive water was removed under reduced pressure upon heating at 80 ^oC. Then, the product was dried at 120 ^oC for 24 h in an oven to give the zirconium or hafnium oxychloride complex as a white solid.

For zirconium oxychloride complex: mp. > 300 ^oC, 500 mg, yield: 98%. Anal. Calcd. for $Zr_4Cl_5O_{24}H_{24}$ requires Cl, 18.65%; Found: Cl, 18.88% (X-ray crystal structure: see A. Clearfield, P. A. Vaughan, *Acta Crystallogr.* **1956**, *9*, 555).

For hafnium oxychloride complex: mp. > 300 ^oC, 487 mg, yield: 96%. Anal. Calcd. for $Hf_4Cl_5O_{24}H_{24}$ requires Cl, 13.64%; Found: Cl, 14.99%.

The single crystal of this complex was obtained by recrystallization from water. Therefore, this complex contains water in its crystal structure. The crystal data of hafnium oxychloride complex has been deposited in FIZ Karlsruhe with number CSD 414059. Empirical Formula: $H_{72}Cl_5O_{48}Hf_4$; Formula Weight: 1731.79; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.366 x 0.273 x 0.186 mm; Crystal System: Tetragonal; Lattice Type: Primitive; Lattice Parameters: a= 17.0031(11)Å, b= 17.0031(11)Å, c= 7.6897(7)Å, α= 90^o, β= 90^o, γ= 90^o, V= 2223.1(3)Å^3; Space group: P4/mnc; Z= 2; D_{calc}= 1.909 g/cm^3; F_{000}= 1152; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0808, 0.2076.

General Procedure for the Nitration of Phenolic Compounds.

Montmorillonite KSF (500 mg) was put into a glass vessel and then heated at 120 ^oC for 0.5 h under reduced pressure (0.1 mm Hg) to get rid of the absorbed water. A solution of resorcinol (110 mg, 1.0 mmol) and hafnium compound (20 mg) in THF (or other solvent, 5 mL) was added into the glass vessel. Nitric acid (60%, 0.095 mL, d = 1.3667, 1.2 mmol) was slowly added dropwise and the mixture was stirred for 16 hours at room temperature. The reaction mixture was extracted with ethyl acetate ($MeCO_2Et$) or dichloromethane (CH_2Cl_2). The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatograph (eluent: petroleum ether/EtOAc = 10/l) to give the product as a yellow solid: 135 mg, yield 87%.

4-Nitroresorcinol 1.

A yellow solid: 135 mg, yield 87%, m.p. 117-119 ^{o}C, IR (KCl) ν 1532, 1397 cm^{-1} (NO_2), 3354, 1255 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 6.47 (1H, dd, J = 9.2 Hz, 3.4 Hz, Ar), 6.52 (1H, d, J = 3.4 Hz, Ar), 8.05 (1H, d, J = 9.2 Hz, Ar), 10.97 (1H, s, ArOH); MS (EI) m/z 155 (M^+, 47.40), 125 (M^+-30, 100), 97 (M^+-58, 94.90), 77 (M^+-78, 6.77) 51 (M^+-104, 65.02); Anal. Calcd. for $C_6H_5NO_4$ (%): requires C, 46.46; H, 3.25; N, 9.03%. Found: C, 46.48; H, 3.44; N, 9.02%.

2-Nitrophenol 2a.

A yellow solid: 56 mg, yield 40%, m.p. 45-47 ^{o}C, IR ($CHCl_3$) ν 1522, 1416 cm^{-1} (NO_2), 3250, 1240 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.00 (1H, dt, J = 7.5 Hz, 1.5 Hz, Ar), 7.16 (1H, d, J = 7.4 Hz, Ar), 7.59 (1H, dt, J = 7.5 Hz, 1.5 Hz, Ar), 8.12 (1H, dd, J = 7.5 Hz, 1.5 Hz, Ar), 10.60 (1H, s, ArOH); MS (EI) m/z 139 (M^+, 100), 122(M^+-17, 6.46), 109 (M^+-30, 22.97), 93 (M^+-46, 8.40); HRMS (EI) Calcd. For $C_6H_5NO_3$ requires M, 139.0269, Found: 139.0272(M^+).

4-Nitrophenol 2a'.

A yellow solid: 61 mg, yield 44%, m.p. 117-119 ^{o}C, IR (KCl) ν 1522, 1416 cm^{-1} (NO_2), 3253, 1240 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 6.08 (1H, s, ArOH), 6.92 (2H, dd, J = 7.1 Hz, 2.1 Hz, Ar), 8.18 (2H, dd, J = 7.1 Hz, 2.0 Hz, Ar); MS (EI) m/z 139 (M, 100), 123 (M^+-16, 4.20), 109 (M^+-30, 47.59), 93 (M^+-46, 19.14); Anal. Calcd. for $C_6H_5NO_3$ (%): requires C, 51.80; H, 3.62; N, 10.07%. Found: C, 51.73; H, 3.73; N, 10.04%.

4-Chloro-2-nitrophenol 2b.

A yellow solid: 170 mg, yield 98%, m.p. 86-88 ^{o}C, IR (KCl) ν 1522, 1416 cm^{-1} (NO_2), 3263, 1240 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.14 (1H, d, J = 9.4 Hz, Ar), 7.54 (1H, dd, J = 9.4 Hz, 2.5 Hz, Ar), 8.11 (1H, d, J = 2.5 Hz, Ar), 10.48 (1H, s, ArOH); MS (EI) m/z 173 (M^+,100), 156 (M^+-17, 9.26), 143 (M^+-30, 9.73), 127 (M^+-46, 15.36); Anal. Calcd. for $C_6H_4ClNO_3$ (%): requires C, 41.52; H, 2.32; N, 8.07%. Found: C, 41.58; H, 2.36; N, 8.10%.

4-Fluoro-2-nitrophenol 2c.

A yellow solid: 134 mg, yield: 86%, m.p. 75-77 ^{o}C, IR (KCl) ν 1526, 1344 cm^{-1} (NO_2), 3265, 1255 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.17 (1H, dd, J = 9.4 Hz, 4.3 Hz, Ar), 7.37 (1H, ddd, J = 9.4 Hz, 7.4 Hz, 3.0 Hz, Ar), 7.83 (1H, dd, J = 8.1 Hz, 3.0 Hz, Ar), 10.38 (1H, s, ArOH); MS (EI) m/z 157 (M^+, 100), 140 (M^+-17, 7.20), 127 (M^+-30, 11.07), 111 (M^+-46, 5.75); Anal. Calcd. for $C_6H_4FNO_3$ (%): requires C, 45.87; H, 2.57; N, 8.92%. Found: C, 46.01; H, 2.58; N, 8.94%.

4-Bromo-2-nitrophenol 2d.

A yellow solid: 180 mg, yield 84%, m.p. 88-90 ^{o}C, IR (KCl) ν 1532, 1412 cm^{-1} (NO_2), 3266, 1249 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.08 (1H, d, J = 9.2 Hz, Ar), 7.67 (1H, dd, J = 9.2 Hz, 2.5 Hz, Ar), 8.26 (1H, d, J = 2.5 Hz, Ar), 10.49 (1H, s, ArOH); MS (EI) m/z 219 (M^+, 100), 202 (M^+-17, 14.58), 189 (M^+-30, 15.72), 173 (M^+-46, 23.19); Anal. Calcd. for $C_6H_4BrNO_3$ (%): requires C, 33.06; H, 1.85; N, 6.42%. Found: C, 33.34; H, 2.08; N, 6.35%.

4-*tert*-Butyl-2,6-dinitrophenol 3e.

A yellow solid: 135 mg, yield 57%, m.p. 96-98 ^{o}C, IR (KCl) ν 1532, 1367 cm^{-1} (NO_2), 3247, 1265 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.37 (9H, s, CH_3), 8.32 (2H, s, Ar), 11.29 (1H, s, ArOH); MS (EI) m/z 240 (M^+, 10.36), 225 (M^++1-16, 100), 197 (M^+-43, 9.31), 179 (M^+-61, 12.85), 77 (M^+-163, 6.69); Anal. Calcd. for $C_{10}H_{12}N_2O_5$ (%): requires C, 50.00; H, 5.04; N, 11.66%. Found: C, 50.07; H, 5.06; N, 11.59%.

4-*tert*-Butyl-2-nitrophenol 2e.

A yellow solid: 78 mg, yield 40%, m.p. 70-73 ^{o}C, IR ($CHCl_3$) ν 1532, 1397 cm^{-1} (NO_2), 3249, 1255 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.33 (9H, s, CH_3), 7.11 (1H, d, J = 9.8 Hz, Ar), 7.65 (1H, dd, J = 9.8 Hz, 3.4 Hz, Ar), 8.08 (1H, d, J = 3.4 Hz, Ar), 10.47 (1H, s, ArOH); MS (EI) m/z 195 (M^+, 16.06), 180 (M^++1-16, 100), 134 (M^+-61, 17.32), 77 (M^+-118, 9.29); HRMS (EI) Calcd. For $C_{10}H_{13}NO_3$ requires M, 195.0895, Found: 195.0899 (M^+).

4-Methoxy-2,6-dinitrophenol 3f.

A yellow solid: 134 mg, yield 73%, m.p. 77-79 ^{o}C, IR (KCl) ν 1537, 1358 cm^{-1} (NO_2), 3251, 1243 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.91 (3H, s, OCH_3), 7.86 (2H, s, Ar), 11.00 (1H, s, ArOH); MS (EI) m/z 214 (M^+, 100), 184 (M^+-30, 5.77), 77 (M^+-137, 18.05), 51 (M^+-163, 30.71); Anal. Calcd. for $C_7H_6N_2O_6$ (%): requires C, 39.26; H, 2.82; N, 13.08%. Found: C, 39.38; H, 2.69; N, 12.87%.

1,4-Dimethoxy-2-nitrobenzene 2g.

A yellow solid: 155 mg, yield 84%, m.p. 71-72 ^{o}C, IR (KCl) ν 1527, 1354 cm^{-1} (NO_2); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.71 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 6.91 (1H, d, J = 9.6 Hz, Ar), 7.01 (1H, dd, J = 9.6 Hz, 3.1 Hz, Ar), 7.28 (1H, d, J = 9.6 Hz, Ar); MS (EI) m/z 183 (M^+, 100), 168 (M^++1-16, 5.88), 136 (M^+-47, 12.08), 122 (M^+-61, 29.74), 107 (M^+-76, 62.06), 77 (M^+-106, 64.71) ; Anal. Calcd. for $C_8H_9NO_4$ (%): requires C, 52.46; H, 4.95; N, 7.65%. Found: C, 52.49; H, 4.95; N, 7.62%.

4-Methyl-2-nitrophenol 4h.

A yellow solid: 122 mg, yield: 81%, m.p. < 40 ^{o}C, IR (KCl) ν 1630, 1370 cm^{-1} (NO_2), 3250, 1245 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.34 (3H, s, CH_3), 7.05 (1H, d, J = 8.2 Hz, Ar), 7.39 (1H, dd, J = 2.0 Hz, 8.2 Hz, Ar), 7.90 (1H, d, J = 2.0 Hz, Ar), 10.44 (1H, s, ArOH); MS (EI) m/z 153 (M^+, 100), 136 (M^+-17, 5.37), 123 (M^+-30, 6.98), 77 (M^+-76, 40.38); Anal. Calcd. for $C_7H_7NO_3$ (%): requires C, 54.90; H, 4.61; N, 9.15%. Found: C, 54.77; H, 4.72; N, 9.30%.

4-Methyl-2,6-dinitrophenol 5h.

A yellow solid: 11 mg, yield: 6%, m.p. 84-86 ^{o}C, IR (KCl) ν 1625, 1360 cm^{-1} (NO_2), 3230, 1237 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.45 (3H, s, CH_3), 8.15 (2H, s, Ar), 11.28 (1H, s, ArOH); MS (EI) m/z 198 (M^+, 100), 106 (M^+-92, 8.49), 77 (M^+-104, 46.87), 43 (M^+-138, 15.82); Anal. Calcd. for $C_7H_6N_2O_5$ (%): requires C, 42.43; H, 3.05; N, 14.14%. Found: C, 42.34; H, 3.14; N, 14.21%.

3-Methyl-4-nitrophenol 4i.

A yellow solid: 88 mg, yield: 58%, m.p. 128-130 ^{o}C, IR (KCl) ν 1600, 1410 cm^{-1} (NO_2), 3170, 1230 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.65 (3H, s, CH_3), 5.99 (1H, s, ArOH), 6.74-6.77 (2H, m, Ar), 8.03-8.07 (1H, m, Ar); MS (EI) m/z 153 (M^+, 55.90), 136 (M^+-17, 100), 123 (M^+-30, 6.24), 77 (M^+-76, 77.06); Anal. Calcd. for $C_7H_7NO_3$ (%): requires C, 54.90; H, 4.61; N, 9.15%. Found: C, 54.65; H, 4.49; N, 9.32%.

5-Methyl-2-nitrophenol 4i'.

A yellow solid: 38 mg, yield: 20%, m.p. 56-58 ^{o}C, IR (KCl) ν 1590, 1360 cm^{-1} (NO_2), 3277, 1274 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.40 (3H, s, CH_3), 6.79 (1H, dd, J = 1.8 Hz, 7.8 Hz, Ar), 6.94 (1H, d, J = 1.8 Hz, Ar), 7.98 (1H, d, J = 7.8 Hz, Ar), 10.62 (1H, s, ArOH); MS (EI) m/z 153 (M^+, 100), 123 (M^+-30, 24.42), 77 (M^+-76, 49.13); Anal. Calcd. for $C_7H_7NO_3$ (%): requires C, 54.90; H, 4.61; N, 9.15%. Found: C, 54.79; H, 4.66; N, 9.28%.

2-Methyl-6-nitrophenol 4j.

A yellow solid: 70 mg, yield: 46%, m.p. 71-73 ^{o}C, IR (KCl) ν 1635, 1344 cm^{-1} (NO_2), 3267, 1236 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.34 (3H, s, CH_3), 6.88 (1H, dd, J = 9.0 Hz, 7.3 Hz, Ar), 7.45 (1H, d, J = 7.3 Hz, Ar), 7.69 (1H, d, J = 9.0 Hz, Ar), 10.92 (1H, s, ArOH); MS (EI) m/z 153 (M^+, 100), 136 (M^+-17, 7.81), 123 (M^+-30, 8.90), 77 (M^+-104, 84.40); Anal. Calcd. for $C_7H_7NO_3$ (%): requires C, 54.90; H, 4.61; N, 9.15%. Found: C, 54.97; H, 4.69; N, 9.07%.

2-Methyl-4-nitrophenol 4j'.

A yellow solid: 55 mg, yield: 36%, m.p. 142-145 ^{o}C, IR (KCl) ν 1626, 1374 cm^{-1} (NO_2), 3237, 1286 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.32 (3H, s, CH_3), 5.83 (1H, s, ArOH), 6.83 (1H, d, J = 9.0 Hz, Ar), 8.02 (1H, dd, J = 9.0 Hz, 2.8 Hz, Ar), 8.07 (1H, d, J = 2.8 Hz, Ar); MS (EI) m/z 153 (M^+, 100), 137 (M^+-16, 4.18), 123 (M^+-30, 52.82), 77 (M^+-104, 79.40); Anal. Calcd. for $C_7H_7NO_3$ (%): requires C, 54.90; H, 4.61; N, 9.15%. Found: C, 54.68; H, 4.58; N, 9.24%.

2-Methyl-4,6-dinitrophenol 5j.

A yellow solid: 8 mg, yield: 4%, m.p. 125-128 ^{o}C, IR (KCl) ν 1643, 1377 cm^{-1} (NO_2), 3237, 1290 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.62 (3H, s, CH_3), 6.82-7.09 (1H, m, Ar), 7.21-7.37 (1H, m, Ar), 7.84 (1H, s, Ar), 10.35 (1H, s, ArOH); MS (EI) m/z 198 (M^+, 100), 152 (M^+-46, 5.13), 121 (M^+-77, 44.02), 105 (M^+-93, 42.50), 77 (M^+-121, 27.37); Anal. Calcd. for $C_7H_6N_2O_5$ (%): requires C, 42.43; H, 3.05; N, 14.14%. Found: C, 42.65; H, 3.17; N, 13.75%.

2-Chloro-6-nitrophenol 6a.

A yellow solid: 60 mg, yield 35%, m.p. 70-71 ^{o}C, IR (KBr) ν 1531, 1324 cm^{-1} (NO_2), 3469, 1259 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 6.97 (1H, dd, *J* = 7.8 Hz, 8.4 Hz, Ar), 7.71 (1H, dd, *J* = 7.8 Hz, 1.5 Hz, Ar), 8.06 (1H, dd, *J* = 8.4 Hz, 1.5 Hz, Ar), 11.03 (1H, s, ArOH); MS (EI) m/z 173 (M^+, 91.92), 143 (M^+-30, 51.06), 115 (M^+-58, 34.80), 99 (M^+-74, 51.49), 91 (M^+-82, 28.13), 73(M^+-100, 28.56) , 63(M^+-110, 100.00),51(M^+-122, 20.60); Anal. Calcd. for $C_6H_4ClNO_3$ (%): requires C, 41.52; H, 2.32; N, 8.07%. Found: C, 41.63; H, 2.28; N, 7.91%.

2-Chloro-4-nitrophenol 7a.

A yellow solid: 107 mg, yield 62%, m.p. 110-112 ^{o}C, IR (KBr) ν 1508, 1335 cm^{-1} (NO_2), 3370, 1252 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.14 (1H, d, *J* = 9.3 Hz, Ar), 8.12 (1H, dd, *J* = 9.3 Hz, 2.7 Hz, Ar), 8.30 (1H, d, *J* = 2.7 Hz, Ar), 6.44 (1H, s, ArOH); MS (EI) m/z 173 (M^+, 100.00), 143 (M^+-30, 75.68), 127 (M^+-46, 19.08), 99 (M^+-74, 64.08), 91 (M^+-82, 35.11), 73(M^+-100, 34.53), 63(M^+-110, 64.71), 53(M^+-120, 21.60); Anal. Calcd. for $C_6H_4ClNO_3$ (%): requires C, 41.52; H, 2.32; N, 8.07%. Found: C, 41.54; H, 2.36; N, 7.92%.

1,2-Diethoxy-4-nitrobenzene 7b.

A yellow solid: 194 mg, yield 92%, m.p. 75-77 ^{o}C, IR (KBr) ν 1520, 1327 cm^{-1} (NO_2); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.50 (3H, t, CH_3), 1.51 (3H, t, CH_3), 4.16 (2H, q, CH_2), 4.19 (2H, q, CH_2), 6.89 (1H, d, *J* = 9.0 Hz, Ar), 7.71 (1H, d, *J* = 2.4 Hz, Ar), 7.85 (1H, dd, *J* =

9.0 Hz, 2.4 Hz, Ar); MS (EI) m/z 211 (M^+, 70.49), 183 (M^+-28, 31.04), 155 (M^+-56, 100.00), 125 (M^+-86, 45.36), 79 (M^+-132, 18.17), 51 (M^+-160, 16.52); Anal. Calcd. for $C_{10}H_{13}NO_4$ (%): requires C, 56.86; H, 6.20; N, 6.63%. Found: C, 56.70; H, 6.20; N, 6.58%.

2-Ethoxy-6-nitrophenol 6c.

A yellow solid: 96 mg, yield 45%, m.p. 62-64 ^oC, IR (KBr) ν 1547, 1328 cm^{-1} (NO_2), 3170, 1249 cm^{-1} (OH); ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.51 (3H, t, CH_3), 4.15 (2H, q, CH_2), 6.89 (1H, dd, *J* = 8.4 Hz, 7.8Hz, Ar), 7.71 (1H, d, *J* = 7.8 Hz, Ar), 7.85 (1H, d, *J* = 8.4 Hz), 10.73 (1H, s, ArOH); MS (EI) m/z 183 (M^+, 39.15), 155 (M^+-28, 29.51), 107 (M^+-76, 100.00), 93 (M^+-90, 22.30), 79 (M^+-104, 28.93), 51 (M^+-132, 23.57); Anal. Calcd. for $C_8H_9NO_4$ (%): requires C, 52.46; H, 4.95; N, 7.65%. Found: C, 52.50; H, 4.91; N, 7.62%.

2-Ethoxy-4-nitrophenol 7c.

A yellow solid: 112 mg, yield 53%, m.p. 95-97 ^oC, IR (KBr) ν 1523, 1338 cm^{-1} (NO_2), 3458, 1263 cm^{-1} (OH); ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.50 (3H, t, CH_3), 4.21 (2H, q, CH_2), 6.97 (1H, d, *J* = 8.7 Hz, Ar), 7.71 (1H, d, *J* = 2.7 Hz, Ar), 7.85 (1H, dd, *J* = 8.7 Hz, 2.7 Hz, Ar), 6.50 (1H, s, ArOH); MS (EI) m/z 183 (M^+,94.89), 155 (M^+-28, 100.00), 125 (M^+-58, 59.82), 109 (M^+-74, 28.60), 81 (M^+-102, 23.68), 52 (M^+-131, 20.45); Anal. Calcd. for $C_8H_9NO_4$ (%): requires C, 52.46; H, 4.95; N, 7.65%. Found: C, 52.77; H, 4.94; N, 7.67%.

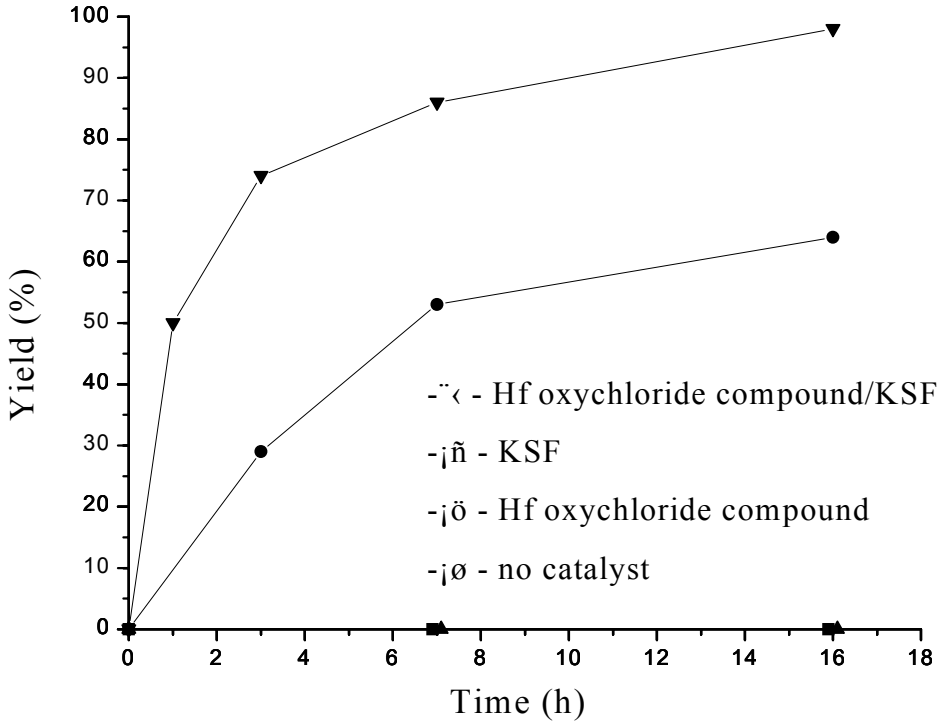

Figure S1. The yields of nitrated *p*-chlorophenol versus time.