Nitro-Group-Directed Selective Deacylation and Desulfonation

Xiujie Ji, Chunbao Li*

Department of Chemistry, Tianjin University, Tianjin 300072, P. R. of China
Fax +86(22)27403475; E-mail: lichunbao@tju.edu.cn

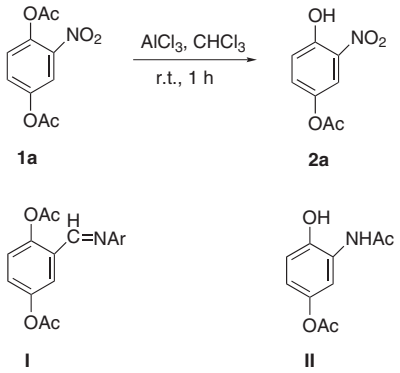
Received 14 February 2006; revised 15 March 2006

Abstract: Nitro-substituted phenolic esters and sulfonates were successfully and selectively deacylated and desulfonated, respectively. The directing effect of the nitro group is supported by the excellent regioselectivities and good yields. These reactions demonstrate for the first time that the complexation of $AlCl_3$ with the phenolic nitro group is stronger than that with the phenolic ester or sulfonate group alone. The mechanism for the selective deacylation and desulfonation directed by the nitro group is proposed.

Key words: selective deacylation, selective desulfonation, nitro group, $AlCl_3$, complexation

It is well documented that phenolic esters undergo Fries rearrangement to produce *o*- and *p*- acylphenols.[1–4] This is the most commonly used method for preparing hydroxy aromatic ketones. The catalyst used in this reaction is usually $AlCl_3$, a Lewis acid. It is known that Lewis acids are capable of coordinating to atoms bearing a lone pair or a partial negative charge such as in amino, imino and nitro groups,[5] which are Lewis bases. For phenolic esters bearing these groups, a different complexation from that required for the Fries reaction could be speculated to predominate, and different products other than the hydroxy aromatic ketones from the Fries rearrangement would be expected. We believe that a nitro group could direct a selective deacylation or desulfonation in phenolic esters, although Fries rearrangement of esters of 2-nitroresorcinol leading to the normal product, e.g. hydroxyl aromatic ketone in moderate yields has been reported.[3,4] However we believe that $AlCl_3$ should coordinate more strongly to the oxygen atoms in the nitro group and in the neighboring ester group than it does to an isolated phenolic ester. This type of complexation would lead to selective deacylation and desulfonation, which have not previously been investigated. This work studies these reactions and proposes a mechanism for them.

We started by subjecting **1a**, **I**, **II** (Scheme 1) to the action of $AlCl_3$. At temperatures from 0 °C to 60 °C in anhydrous chloroform, no reactions took place for **I** and **II**. We were delighted to find that **1a** was selectively deacylated into **2a** when **1a** was treated with $AlCl_3$ (1.0 equiv) at 20 °C (Scheme 1).



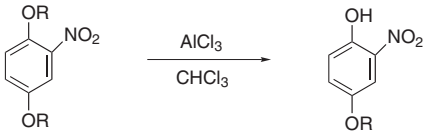
Scheme 1 Selective deacetylation on substrates **1a**, **I** and **II**

Similarly, a series of substrates **1** and **3** (Schemes 2 and 3) were all selectively deacylated or desulfonated in high yields and at high reaction rates except for the failure of the selective demesylation of **1i** (Scheme 2). Thus a series of nitro-substituted phenolic esters and sulfonates **2** and **4** (Schemes 2 and 3) was synthesized and these compounds are shown in Tables 1 and 2. In all cases, the regioselectivity is excellent and we did not detect any regioisomers. All the products were characterized spectroscopically. The IR (3220–3430 cm^{-1}) and ^1H NMR (10.45–10.76 ppm) spectra display typical intramolecular hydrogen bonding.

On replacing $AlCl_3$ with other Lewis acid such as BF_3, $ZrCl_4$, and $FeCl_3$, we found that the reaction rates were tremendously decreased. To further demonstrate the neighboring nitro group effect, we prepared *o*-nitrophenyl acetate, *m*-nitrophenyl acetate and *p*-nitrophenyl acetate. The three acetates were similarly treated with $AlCl_3$ at room temperature for 24 hours. Only *o*-nitrophenyl acetate afforded the desired product, *o*-nitrophenol, in 85% yield. In contrast, the other two acetates did not react at all. When an alkyl nitro acetate, 1-nitro-2-butyl acetate, was treated with $AlCl_3$, the reaction was very sluggish. The starting materials remained practically unchanged after two days with small amount of side-products and no desired deacylation products were detected.

The substrates **1a–f**, **3a–e** (Schemes 2 and 3) were prepared by the diacylation of 2-nitrohydroquinone and 4-nitroresorcinol using the corresponding acyl chloride and anhydrous triethylamine in anhydrous chloroform.[3,4] Similarly, the substrates **1g–i**, **3f** and **3g** (Schemes 2 and 3) were prepared by the disulfonation of 2-nitrohydroquinone and 4-nitroresorcinol using the corresponding sulfo-

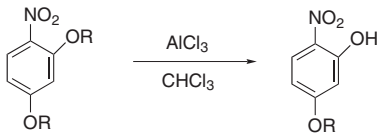
SYNTHESIS 2006, No. 15, pp 2478–2482
Advanced online publication: 28.06.2006
DOI: 10.1055/s-2006-942451; Art ID: F02206SS



1 2

1a, **2a**: R = MeCO
1b, **2b**: R = EtCO
1c, **2c**: R = $Me(CH_2)_3CO$
1d, **2d**: R = $Me(CH_2)_{16}CO$
1e, **2e**: R = PhCO
1f, **2f**: R = *o*-Cl-C_6H_4CO
1g, **2g**: R = $PhSO_2$
1h, **2h**: R = Ts **1i**: R = Ms

Scheme 2 Selective deacylation and desulfonation of **1**



3 4

3a, **4a**: R = MeCO
3b, **4b**: R = EtCO
3c, **4c**: R = $Me(CH_2)_{16}CO$
3d, **4d**: R = PhCO
3e, **4e**: R = *o*-Cl-C_6H_4CO
3f, **4f**: R = $PhSO_2$
3g, **4g**: R = Ts

Scheme 3 Selective deacylation and desulfonation of **3**

nyl chloride and anhydrous triethylamine in anhydrous chloroform.[3,4]

By comparing the reaction rates of the deacylation and desulfonation, a general mechanism represented by desulfonation can be proposed (Scheme 4). In most cases, the selective reaction of aliphatic esters needed 1.0–2.0 equivalents of $AlCl_3$, and took less than ten hours at room temperature for completion. Except for aromatic carboxylic esters and aromatic sulfonates, higher reaction temperatures and longer reaction times are needed. This can be attributed to the stabilization of the carbonyl cation by the electron-donating alkyl groups. $RCO^+ AlCl_4^-$ is less electrophilic towards the phenolic hydroxy group than $ArCO^+ AlCl_4^-$. This in turn reduces the esterification reaction (the reverse reaction). For desulfonation (Scheme 4), the limiting step is the formation of sulfonic chloride via the attack of the chloride ion on the sulfur. The more positively charged the sulfur, the faster the desulfonation. Therefore

Table 1 Selective Deacylation of **1a–f** and Selective Desulfonation of **1g–i** Using $AlCl_3$

Entry	Product	$AlCl_3$ (equiv)	Temp (°C)	Time (h)	Yield (%)[a]	mp (°C)
1	**2a**	1.0	20	1	85	80–81 (84[6])
2	**2b**	1.5	20	1.5	91	58–60
3	**2c**	1.5	20	2.5	80	36–38
4	**2d**	2.0	20	3.5	92	60–62
5	**2e**	2.0	20	17	81	95–97 (95.5–97.5[7])
6	**2f**	2.0	20	3	83	132–134
7	**2g**	2.0	20	7	91	69–71
8	**2h**	2.0	20	12	88	107–109
9	**2i**	2.0	60	24	NR	

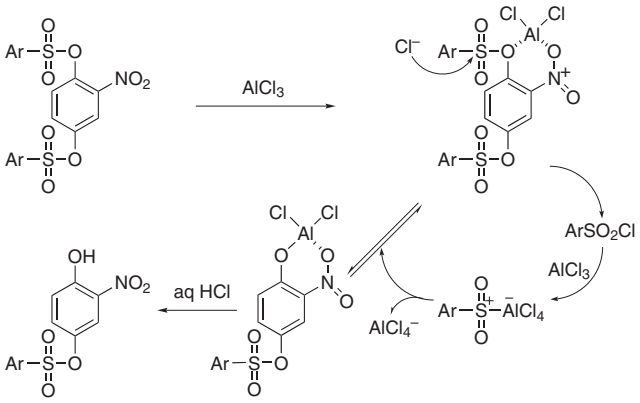
[a] Yield of isolated product.

Table 2 Selective Deacylation of **3a–e** and Selective Desulfonation of **3f** and **3g** Using $AlCl_3$

Entry	Product	$AlCl_3$ (equiv)	Temp (°C)	Time (h)	Yield (%)[a]	mp (°C)
1	**4a**	1.0	20	1	73	86–88
2	**4b**	1.5	20	3	81	63–65
3	**4c**	2.0	20	3.5	82	56–58
4	**4d**	2.0	20	10	85	121–123 (124[8])
5	**4e**	2.0	20	3	71	114–116
6	**4f**	2.0	60	1.5	77	78–80
7	**4g**	2.0	20	6	77	87–89

[a] Yield of isolated product.

we observed benzenesulfonate was desulfonated much faster than tosylate (Table 1, entries 7, 8 and Table 2, entries 5, 6). In mesylate, the electron-donating methyl group makes the sulfur less positively charged than in arylsulfonate. We could not detect any trace amount of demesylation product when substrate **1i** was treated with $AlCl_3$ at 60 °C for 24 hours (Table 1, entry 9).



Scheme 4 Proposed mechanism represented by selective desulfonation using $AlCl_3$

Most of the deacylated compounds are useful intermediates.[6–15] For example, 4-hydroxy-3-nitrophenyl acetate (**2a**) was used in synthesizing bioactive compounds[9] such as calcium ion indicators.[12] 4-Hydroxy-3-nitrophenyl benzoate (**2e**) is a useful intermediate for a new material with a higher concentration of nonlinear optics chromophores.[10] Acetate **2a** has been made by refluxing substrate 1,4-diacetoxybenzene **1a** for four hours with ceric ammonium nitrate (CAN) in methanol in 40% yield.[16] It has also been produced as a by-product when **1a** was treated with fuming nitric acid at 5–8 °C[6] or with peroxynitrite, $FeCl_3$ and ethylenediaminetetraacetic acid (EDTA) in aqueous phosphate buffer.[13] 3-Hydroxy-4-nitrophenyl benzoate (**4d**) has been obtained in 33% yield when 3-benzoxyphenol was treated with nitric acid in glacial acetic acid[17] or in 38% yield with concentrated nitric acid in acetic acid.[8]

Selective desulfonation of polyphenolic sulfonates has never been realized before. This represents the first selective desulfonation procedure of polyphenolic sulfonates. The products of the selective desulfonation are new types of compounds. The hydroxyl group is electron-donating, especially under basic conditions. We speculate that this would dramatically influence the behavior of the aryl carbon and the sulfonoxy oxygen bond and find applications in organic synthesis. One of the possible applications is in the modified Suzuki reaction,[18–21] where the reaction rate would be dramatically improved due to the electron-donating effect of the hydroxyl group. We have started this investigation.

In conclusion, we have established a new procedure for the selective deacylation and desulfonation of polyphenolic esters directed by a nitro group. These reactions demonstrate that a nitro group on a phenolic ester has a better ability to complex with $AlCl_3$ than an isolated phenolic ester group does (Fries rearrangement). The regioselectivity is excellent and the reaction rates and yields are high. The products are useful intermediates in organic synthesis. The products from the selective desulfonation represent a new type of compounds.

All moisture-sensitive reactions were performed in flame-dried glassware. Triethylamine and chloroform were dried over NaOH and P_2O_5, respectively and distilled prior to use. $AlCl_3$ were sublimed prior to use. Other reagents were purified by standard laboratory procedure. All organic extracts were dried over Na_2SO_4. The boiling point range of PE used in flash chromatography and crystallization was 60–90 °C. The products were purified by crystallization or flash column chromatography. Silica gel 60 (200–300 mesh) and silica gel 60 F254 were used for column chromatography and analytical TLC, respectively. Melting points were determined on a Reichert hot-stage apparatus and are uncorrected. IR spectra were determined on a Bio-Rad FTS3000 spectrometer. NMR spectra were recorded on Bruker AC 400 or Varian INOVA500 spectrometers. Mass spectral data (ESI–MS) were obtained from Finnigan LCQ Advatage MAX spectrometer. Microanalyses were performed with Vanio-EL Analysensysteme Gmbl analyzer.

Selective Deacylation and Desulfonation; Typical Procedure

The substrate **1** or **3** (1 mmol) was dissolved in anhyd $CHCl_3$ (30 mL) and cooled to 0 °C. After $AlCl_3$ (1.0–2.0 equiv) was added in portions within 0.5 h, the reaction was allowed to warm to r.t. or refluxed (as indicated in the Tables 1 and 2). Upon addition of $AlCl_3$ the reaction solution became red. The reaction was monitored via TLC. When the substrate disappeared, the reaction was cooled to r.t., and reaction mixture was treated with 10% aq HCl, extracted with CH_2Cl_2 (3 × 50 mL), dried with Na_2SO_4 and concentrated. The residue was purified by crystallization or flash column chromatography.

4-Hydroxy-3-nitrophenyl Propionate (2b)

Yield: 91%; yellow needles; mp 58–60 °C. The product was purified by flash column chromatography using PE–EtOAc (15:1) and crystallization with PE.

IR (KBr): 3386, 3089, 2947, 2925, 1765, 1549, 1244, 1138, 940, 794 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.6 Hz, 3 H), 2.61 (q, *J* = 7.6 Hz, 2 H), 7.17 (d, *J* = 9.2 Hz, 1 H), 7.35 (dd, *J* = 2.8, 9.2 Hz, 1 H), 7.87 (d, *J* = 2.8 Hz, 1 H), 10.50 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.10, 27.76, 117.69, 120.81, 131.84, 133.84, 143.16, 153.00, 172.78.

ESI–MS: *m*/*z* = 211 [M^+ + 1].

Anal. Calcd for $C_9H_9NO_5$: C, 51.19; H, 4.30; N, 6.63. Found: C, 51.27; H, 4.45; N, 6.53.

4-Hydroxy-3-nitrophenyl Valerate (2c)

Yield: 80%; yellow needles, mp 36–38 °C. The product was purified by flash column chromatography using PE–Et_2O (3:1) and crystallization with PE.

IR (KBr): 3269, 3098, 2960, 2935, 1765, 1539, 1239, 1137, 1099, 944, 843 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.0 Hz, 3 H), 1.45–1.49 (m, 2 H), 1.75–1.78 (m, 2 H), 2.59 (t, *J* = 7.5 Hz, 2 H), 7.20 (d, *J* = 9.5 Hz, 1 H), 7.36 (dd, *J* = 2.0, 9.0 Hz, 1 H), 7.88 (d, *J* = 3.5 Hz, 1 H), 10.50 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.82, 22.41, 27.06, 34.06, 117.68, 120.80, 129.06, 131.87, 143.15, 153.00, 172.12.

ESI–MS: m/z = 239 [M^+ + 1].

Anal. Calcd for $C_{11}H_{13}NO_5$: C, 55.23; H, 5.48; N, 5.85. Found: C, 55.34; H, 5.63; N, 5.75.

4-Hydroxy-3-nitrophenyl Stearate (2d)
Yield: 92%; yellow needles; mp 60–62 °C. The product was purified by crystallizing with EtOH.

IR (KBr): 3293, 3094, 2955, 2918, 1749, 1545, 1245, 1219, 1154, 951, 828 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.2 Hz, 3 H), 1.26–1.41 (m, 28 H), 1.75 (t, J = 7.6 Hz, 2 H), 2.56 (t, J = 7.6 Hz, 2 H), 7.16 (d, J = 8.8 Hz, 1 H), 7.34 (dd, J = 2.8, 9.2 Hz, 1 H), 7.86 (d, J = 2.8 Hz, 1 H), 10.45 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.25, 22.87, 25.02, 29.29, 29.41, 29.51, 29.54, 29.63, 29.68, 29.78, 29.81, 29.83, 29.85, 29.86, 29.89, 32.13, 34.37, 110.00, 117.69, 120.80, 131.86, 143.16, 153.00, 172.14.

ESI–MS: m/z = 421 [M^+ + 1].

Anal. Calcd for $C_{24}H_{39}NO_5$: C, 68.38; H, 9.32; N, 3.32. Found: C, 68.42; H, 9.41; N, 3.13.

4-Hydroxy-3-nitrophenyl 2-Chlorobenzoate (2f)
Yield: 83%; yellow needles; mp 132–134 °C. The product was purified by crystallizing with EtOH.

IR (KBr): 3228, 3095, 1742, 1536, 1256, 1101, 1038, 894 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.27 (d, J = 9.5 Hz, 1 H), 7.43–7.45 (m, 1 H), 7.53–7.56 (m, 3 H), 8.05 (d, J = 3.0 Hz, 1 H), 8.06 (d, J = 7.5 Hz, 1 H), 10.55 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 117.86, 121.02, 127.07, 128.72, 131.75, 131.83, 132.20, 133.42, 133.84, 134.89, 143.01, 153.30, 163.89.

ESI–MS: m/z 293 [M^+ + 1].

Anal. Calcd for $C_{13}H_8NO_5Cl$: C, 53.17; H, 2.75; N, 4.77. Found: C, 53.18; H, 2.70; N, 4.72.

4-Hydroxy-3-nitrophenyl Benzenesulfonate (2g)
Yield: 91%; yellow needles; mp 69–71 °C. The product was purified by flash column chromatography using PE–Et_2O (3:1) and crystallization with a mixture of EtOAc and PE.

IR (KBr): 3310, 3089, 1625, 1532, 1243, 1188, 944, 839 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.13 (d, J = 9.0 Hz, 1 H), 7.30 (dd, J = 3.0, 9.0 Hz, 1 H), 7.57–7.62 (m, 2 H), 7.70 (d, J = 3.0 Hz, 1 H), 7.73–7.76 (m, 1 H), 7.88 (d, J = 8.5 Hz, 2 H), 10.51 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 117.82, 121.35, 128.00, 128.74, 129.41, 129.69, 132.34, 135.01, 135.07, 141.63.

ESI–MS: m/z = 295 [M^+ + 1].

Anal. Calcd for $C_{12}H_9SO_6N$: C, 48.81; H, 3.07; N, 4.74. Found: C, 48.83; H, 3.15; N, 4.73.

4-Hydroxy-3-nitrophenyl 4-Toluenesulfonate (2h)
Yield: 88%; yellow needles; mp 107–109 °C. The product was purified by crystallizing with a mixture of EtOAc and PE.

IR (KBr): 3380, 3099, 1539, 1243, 1176, 831 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 7.11 (d, J = 9.2 Hz, 1 H), 7.29 (dd, J = 2.8, 9.2 Hz, 1 H), 7.36 (d, J = 8.4 Hz, 2 H), 7.68 (d, J = 8.4 Hz, 1 H), 7.73 (dd, J = 1.6, 8.4 Hz, 2 H), 10.48 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.92, 118.83, 121.27, 128.78, 130.28, 132.06, 132.43, 133.20, 141.75, 146.34, 153.90.

ESI–MS: m/z = 309 [M^+ + 1].

Anal. Calcd for $C_{13}H_{11}SO_6N$: C, 50.48; H, 3.58; N, 4.53. Found: C, 50.50; H, 3.59; N, 4.50.

3-Hydroxy-4-nitrophenyl Acetate (4a)
Yield: 73%; yellow needles; mp 86–88 °C. The product was purified by flash column chromatography using PE–Et_2O (4:1) and crystallization with PE.

IR (KBr): 3253, 3083, 2946, 1758, 1530, 1204, 1138, 978, 847 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 6.79 (dd, J = 2.5, 7.0 Hz, 1 H), 6.95 (d, J = 2.5 Hz, 1 H), 8.14 (d, J = 6.5 Hz, 1 H), 10.71 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.77, 113.04, 115.03, 127.11, 131.89, 157.00, 158.03, 168.65.

ESI–MS: m/z = 197 [M^+ + 1].

Anal. Calcd for $C_8H_7NO_5$: C, 48.74; H, 3.58; N, 7.10. Found: C, 48.80; H, 3.61; N, 7.08.

3-Hydroxy-4-nitrophenyl Propionate (4b)
Yield: 81%; yellow needles; mp 63–65 °C. The product was purified by flash column chromatography using PE–Et_2O (4:1) and crystallization with PE.

IR (KBr): 3205, 2986, 2945, 1763, 1540, 1264, 1126, 1071, 970, 846 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, J = 7.5 Hz, 3 H), 2.63 (q, J = 7.5 Hz, 2 H), 6.77 (dd, J = 2.5, 9.0 Hz, 1 H), 6.95 (d, J = 2.5 Hz, 1 H), 8.14 (d, J = 9.5 Hz, 1 H), 10.72 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.83, 27.77, 112.36, 114.41, 126.47, 131.19, 156.41, 157.58, 171.62.

ESI–MS: m/z = 211 [M^+ + 1].

Anal. Calcd for $C_9H_9NO_5$: C, 51.19; H, 4.30; N, 6.63. Found: C, 51.25; H, 4.44; N, 6.60.

3-Hydroxy-4-nitrophenyl Stearate (4c)
Yield: 82%; yellow needles; mp 56–58 °C. The product was purified by crystallizing with PE.

IR (KBr): 3213, 3119, 2955, 2921, 1765, 1544, 1262, 1141, 973, 845 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 5.6 Hz, 3 H), 1.26–1.42 (m, 28 H), 1.71–1.81 (m, 2 H), 2.58 (t, J = 7.5 Hz, 2 H), 6.77 (dd, J = 2.5, 9.5 Hz, 1 H), 6.94 (d, J = 2.5 Hz, 1 H), 8.14 (d, J = 9.0 Hz, 1 H), 10.72 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.82, 23.38, 25.38, 29.70, 29.74, 29.89, 30.05, 30.11, 30.27, 30.32, 30.35, 30.36, 30.37, 30.39, 32.61, 34.84, 35.04, 113.06, 115.11, 115.96, 127.14, 157.10, 158.27, 171.64.

ESI–MS: m/z = 421 [M^+ + 1].

Anal. Calcd for $C_{24}H_{39}NO_5$: C, 68.38; H, 9.32; N, 3.32. Found: C, 68.45; H, 9.30; N, 3.29.

3-Hydroxy-4-nitrophenyl 2-Chlorobenzoate (4e)
Yield: 71%; yellow needles; mp 114–116 °C. The product was purified by crystallizing with a mixture of EtOAc and PE.

IR (KBr): 3203, 3118, 1753, 1533, 1234, 1143, 1034, 970, 844 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 6.95 (dd, J = 2.5, 9.0 Hz, 1 H), 7.12 (d, J = 2.5 Hz, 1 H), 7.41–7.44 (m, 1 H), 7.53–7.57 (m, 2 H), 8.05 (d, J = 7.5 Hz, 1 H), 8.21 (d, J = 9.5 Hz, 1 H), 10.76 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 112.59, 114.44, 126.62, 126.92, 127.98, 131.47, 131.62, 132.15, 133.93, 134.82, 156.46, 157.30, 162.55.

ESI–MS: *m*/*z* = 293 [M^+ + 1].

Anal. Calcd for $C_{13}H_8NO_5Cl$: C, 53.17; H, 2.75; N, 4.77. Found: C, 53.28; H, 2.69; N, 4.70.

3-Hydroxy-4-nitrophenyl Benzenesulfonate (4f)
Yield: 77%; yellow needles; mp 78–80 °C. The product was purified by flash column chromatography using PE–Et_2O (3:1) and crystallization with a mixture of Et_2O and PE.

IR (KBr): 3260, 3096, 1621, 1535, 1265, 1194, 973, 876 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.71 (dd, *J* = 9.5 Hz, 1 H), 6.84 (d, *J* = 2.5 Hz, 1 H), 7.59 (t, *J* = 8.0 Hz, 2 H), 7.74 (t, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 7.5 Hz, 2 H), 8.08 (d, *J* = 9.5 Hz, 1 H), 10.64 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 113.11, 114.54, 126.85, 128.41, 129.54, 132.16, 134.88, 134.94, 155.58, 156.19.

ESI–MS: *m*/*z* = 295 [M^+ + 1].

Anal. Calcd for $C_{12}H_9SO_6N$: C, 48.81; H, 3.07; N, 4.74. Found: C, 48.90; H, 3.14; N, 4.70.

3-Hydroxy-4-nitrophenyl 4-Toluenesulfonate (4g)
Yield: 77%; yellow needles; mp 87–89 °C. The product was purified by crystallizing with EtOH.

IR (KBr): 3197, 3093, 2974, 1622, 1534, 1270, 1197, 972, 881 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.48 (s, 3 H), 6.71 (dd, *J* = 2.5, 9.5 Hz, 1 H), 6.85 (d, *J* = 2.5 Hz, 1 H), 7.37 (d, *J* = 7.5 Hz, 2 H), 7.76 (dd, *J* = 2.0, 6.5 Hz, 2 H), 8.08 (d, *J* = 9.5 Hz, 1 H), 10.65 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.78, 113.07, 114.57, 126.81, 128.45, 130.15, 131.94, 132.13, 146.31, 155.77, 156.21.

ESI–MS: *m*/*z* = 309 [M^+ + 1].

Anal. Calcd for $C_{13}H_{11}SO_6N$: C, 50.48; H, 3.58; N, 4.53. Found: C, 50.50; H, 3.64; N, 4.48.

Acknowledgment

We thank NSFC (20572078) and TJU Young Teacher Foundation W50501 for financial support.

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