Preparation of some organic precursors via photolytic demetallation of their iron complexes

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Abstract. Nucleophilic aromatic substitution (S_NAr) of chloroarenes complexed to the cyclopentadienyl iron moiety with ethyl cyanoacetate or phenylsulfonylacetonitrile in the presence of potassium carbonate in DMF resulted in the formation of arylated ethyl cyanoacetate or phenylsulfonylacetonitrile complexes. Photolytic demetallation of these complexes led to the liberation of the substituted arene ligands in high yield. This synthetic route is more advantageous than those previously reported and is a practical way to synthesise heterocycles and alkanolic acid precursors.

Keywords. S_NAr ; photolysis; ethyl arylcyanoacetate; aryl phenylsulfonylacetonitrile.

1. Introduction

There has been considerable interest in the development of new and efficient routes to the synthesis of arylated ethyl cyanoacetates and phenylsulfonylacetonitriles (Shen 1972; Suzuki *et al* 1987; Sakamoto *et al* 1990). These materials are known to be versatile intermediates in the synthesis of heterocyclic compounds (e.g. azetinones, pyrimidines, and oxazaphosphorinane derivatives) and alkanolic acids, which are used for medicinal purposes (Matsui and Motoi 1973; Giordano *et al* 1984; Shih and Wang 1984). One of the well-recognized alkanolic acids is 2-(4-isobutylphenyl)propanoic acid, known as Ibuprofen. This acid is an anti-inflammatory analgesic, finding use in the treatment of patients with rheumatoid arthritis and in relieving general muscle pain and stiffness (Adams *et al* 1969; Chalmers 1969; Shen 1979). The synthesis of ethyl arylcyanoacetates and arylated phenylsulfonylacetonitriles cannot be achieved directly through nucleophilic substitution reactions of ethyl cyanoacetate or phenylsulfonylacetonitrile anions with arylhalides. The routes to these compounds involve the use of certain organometallic reagents or catalysts to promote nucleophilic substitution on the aromatic ring (Kaiser *et al* 1971; Osuka *et al* 1983; Uno *et al* 1985; Sakamoto *et al* 1988; Kozyrod *et al* 1991). In these synthetic routes, the most problematic step is the nucleophilic aromatic substitution.

Activation of normally unreactive chloroarenes towards nucleophilic aromatic substitution reactions (S_NAr) by complexation to a metal moiety such as chromium tricarbonyl, manganese tricarbonyl or cyclopentadienyliron (CpFe) have been

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reported (Semmelhack 1976; Pearson *et al* 1986; Kerber 1991). Nesmeyanov *et al* (1967) were the first to establish the efficient displacement of the chlorine atom in η^6 -chlorobenzene- η^5 -cyclopentadienyliron complex cations by some oxygen, sulfur and nitrogen nucleophiles. We have been very active in utilizing this methodology in the synthesis of various functionalized aromatic compounds (Abd-El-Aziz *et al* 1988, 1993; Abd-El-Aziz and de Denus 1992, 1993).

Nesmeyanov *et al* (1970) examined the effect of irradiation of arene complexes. They found that the photolytic degradation of these complexes in acetonitrile solution resulted in liberation of the arene ligands with ferrocene and iron(II) salt. This photolytic degradation was proven to be greatly dependent on the nature of the solvent, with σ -donor ligands resulting in the greatest yields. Gill and Mann (1980, 1981, 1983) have also given detailed descriptions of the photoinduced replacement of the arene by one 6-electron or three 2-electron ligands.

In this article, we describe our approach to the arylation of ethyl cyanoacetate and phenylsulfonylacetonitrile via S_NAr followed by photolytic demetallation.

2. Results and discussion

η^6 -Chloroarene- η^5 -cyclopentadienyliron hexafluorophosphates (**1a–d**) were prepared via ligand exchange reactions involving ferrocene and chlorobenzene, *o*-, *m*- or *p*-dichlorobenzene according to the method reported by Khand *et al* (1968). Reactions of the product complexes (**1a–d**) with phenylsulfonylacetonitrile or ethyl cyanoacetate in the presence of potassium carbonate in *N,N*-dimethylformamide, led to the formation of complexed arylated ethyl cyanoacetates (**2a–d**) and phenylsulfonylacetonitriles (**3a–d**) as shown in scheme 1. These complexes were isolated as yellow solids or yellow-brown oils in very good yields (71–94%). Ortho substituents on the complexed aromatic ring did not cause any sterically induced inhibition of the reaction. ^1H and ^{13}C NMR and IR were used to characterize the prepared complexes (**2a–d**, **3a–d**). In the ^1H NMR spectra of these complexes, a very distinctive singlet appeared around 5.31–5.47 ppm which is characteristic of the cyclopentadienyl (Cp) ring. For complexes (**3a–d**), in many cases the methine proton appeared at 6–7 ppm overlapping with the arene protons. The assignment of some of these methine protons was based on the integration of the peaks in the region between 6–7 ppm relative to other proton peaks in the spectra. The ^{13}C NMR was also in agreement with expectations, as is outlined in § 3.

(**1a**) $\text{R}^1 = \text{H}$

b: $\text{R}^1 = \text{o-Cl}$

c: $\text{R}^1 = \text{m-Cl}$

d: $\text{R}^1 = \text{p-Cl}$

(**2a–d**) $\text{R}^2 = \text{COOEt}$

(**3a–d**) $\text{R}^2 = \text{SO}_2\text{Ph}$

(**4a–d**) $\text{R}^2 = \text{COOEt}$

(**5a–d**) $\text{R}^2 = \text{SO}_2\text{Ph}$

Scheme 1.

Liberation of the arylated ethyl cyanoacetates and phenylsulfonylacetonitriles from their iron complexes is one of the most important steps in this synthetic strategy. Since photolysis is known to be an efficient method for the decomplexation of some (arene)cyclopentadienyliron complexes, we successfully applied this technique to liberate the free organic ligands. The complexes were dissolved in a mixture of acetonitrile/dichloromethane and irradiated under a nitrogen atmosphere for 2 h, using a Xenon lamp as the source of radiation. Purification of the products by column chromatography resulted in isolation of the free aromatic ligands (4a–d, 5a–d) in yields ranging from 70–84%.

The identities of all photolysed products were confirmed by ^1H and ^{13}C NMR, IR, and MS. The major differences in the ^1H and ^{13}C NMR of these compounds from the complexes are the absence of the cyclopentadienyl peak, the shift of the arene peaks downfield, and a shift of the methine peak to a higher field. Compounds (4a–d) are some of the heterocyclic precursors, and compounds (5a–d) are the desired precursors for some alkanolic acid synthesis. Our synthetic methodology is extremely versatile and efficient in the preparation of such precursors.

In conclusion, we would like to point out that photolysis is an important and efficient step in the synthetic strategy and the $\text{S}_{\text{N}}\text{Ar}$ route to the synthesis of arylated ethyl cyanoacetates and phenylsulfonylacetonitriles is very useful owing to its ease and the use of mild reagents.

3. Experimental

Ethyl cyanoacetate, phenylsulfonylacetonitrile, potassium carbonate and N,N-dimethylformamide (DMF) are commercially available and were used without further purification.

^1H and ^{13}C NMR were recorded on a Gemini 200 NMR spectrometer, with chemical shifts calculated from the solvent signals. MS spectra were recorded on a HP 5970 Series Mass Selective Detector in m/z units. IR spectra were recorded using a Perkin-Elmer 781 spectrophotometer.

3.1 Nucleophilic substitution reactions

(a) *Reactions with ethyl cyanoacetate:* A mixture of 1 mmol of starting cation (1a–d), 2.5 mmol potassium carbonate, and 1.05 mmol of ethyl cyanoacetate in 10 ml of DMF was stirred at 50–60°C, under a nitrogen atmosphere for 3 h. The resulting dark red reaction mixture was filtered into 10 ml of 10% hydrochloric acid. A concentrated aqueous solution of ammonium hexafluorophosphate was added to the reaction mixture, and the product extracted with dichloromethane (3 $\times$ 50 ml). The combined extract was washed with water (4 $\times$ 40 ml), dried over magnesium sulphate, and the solvent was evaporated off under reduced pressure at 25°C. The residual yellow-brown oil was washed with diethyl ether (3 $\times$ 20 ml). Thus the following compounds were prepared.

(b) (η^5 -Cyclopentadienyl) [η^6 -ethyl 2-phenyl cyanoacetate]-iron(II) hexafluorophosphate (2a): (0.362 g, 80%) ν_{max} (cm^{-1}) (neat) 2260 (CN), 1755 (CO); δ_{H} (CD_3COCD_3) 1.24 (3H, t, $J = 7.1$, CH_3), 4.24 (2H, q, $J = 6.7$, CH_2), 5.31 (5H, s, Cp), (5.72 (1H, s, CH), 6.63 (5H, br, s, ArH); δ_{C} (CD_3COCD_3) 13.86 (CH_3), 43.11 (CH), 64.55 (CH_2),

78·83 (5C, Cp), 86·98, 89·09, 89·19, 89·37, 90·21 (5C, ArC), 96·93 (quaternary ArC), 115·33 (CN), 163·70 (CO).

(c) (η^5 -Cyclopentadienyl) [η^6 -ethyl-(*o*-chlorophenyl) cyanoacetate]-iron(II) hexafluorophosphate (**2b**): (0·346 g, 71%) $\nu_{\max}(\text{cm}^{-1})$ (neat) 2305 (CN), 1755 (CO); $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3)$ 1·25 (3H, t, $J = 7·2$, CH_3), 4·30 (2H, q, $J = 6·8$, CH_2), 5·47 (5H, s, Cp), 6·26 (1H, s, CH), 6·71 (1H, t, $J = 6·1$, ArH), 6·85 (2H, m, ArH), 7·05 (1H, d, $J = 7·3$, ArH); $\delta_{\text{C}}(\text{CD}_3\text{COCD}_3)$ 13·76 (CH_3), 41·56 (CH), 64·67 (CH_2), 80·87 (5C, Cp), 87·12, 88·53, 89·71, 89·90 (4C, ArC), 95·30, 108·56 (quaternary ArC), 114·85 (CN), 162·48 (CO).

(d) (η^5 -Cyclopentadienyl) [η^6 -ethyl-(*m*-chlorophenyl) cyanoacetate]-iron(II) hexafluorophosphate (**2c**): (0·365 g, 74%) $\nu_{\max}(\text{cm}^{-1})$ (neat) 2200 (CN), 1760 (CO); $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3)$ 1·26 (3H, t, $J = 7·1$, CH_3), 4·31 (2H, q, $J = 7·1$, CH_2), 5·46 (5H, s, Cp), 5·83 (1H, s, CH), 6·65–7·05 (4H, t, $J = 6·1$, ArH); $\delta_{\text{C}}(\text{CD}_3\text{COCD}_3)$ 13·02 (CH_3), 41·74 (CH), 63·93 (CH_2), 80·28 (5C, Cp), 86·41, 87·98, 88·96, 89·82 (4C, ArC), 96·04, 107·08 (quaternary ArC), 115·26 (CN), 162·45 (CO).

(e) (η^5 -Cyclopentadienyl) [η^6 -ethyl-(*p*-chlorophenyl) cyanoacetate]-iron(II) hexafluorophosphate (**2d**): (0·396 g, 81%) $\nu_{\max}(\text{cm}^{-1})$ (neat) 2310 (CN), 1760 (CO); $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3)$ 1·25 (3H, t, $J = 7·0$, CH_3), 4·25 (2H, q, $J = 7·1$, CH_2), 5·42 (5H, s, Cp), 5·72 (1H, s, CH), 6·74 (2H, d, $J = 5·1$, ArH), 6·97 (2H, d, $J = 6·5$, ArH); $\delta_{\text{C}}(\text{CD}_3\text{COCD}_3)$ 13·07 (CH_3), 41·67 (CH), 63·91 (CH_2), 80·41 (5C, Cp), 86·11, 88·52, 88·55, 88·64 (4C, ArC), 95·34, 107·48, (quaternary ArC), 115·30 (CN), 162·54 (CO).

3.2 Reactions with phenylsulfonylacetonitrile

A mixture of 1 mmol of starting cation (**1a–d**), 2·5 mmol of potassium carbonate, 1·05 mmol phenylsulfonylacetonitrile, and 10 ml of DMF was stirred at room temperature under a nitrogen atmosphere for ≈ 7 h. The resulting red reaction mixture was rapidly filtered into 10% hydrochloric acid (10 ml). The reaction flask was then washed with ethanol and the washing added to the filtrate. The ethanol was removed under reduced pressure at 25°C using a rotary evaporator (Buchi RE-111). A concentrated aqueous solution of ammonium hexafluorophosphate was added to the reaction mixture. The solution was then stirred for 10 min and the resulting yellow product was collected by filtration. Thus the following were prepared.

(a) (η^5 -Cyclopentadienyl) [η^6 -phenyl phenylsulphonylacetonitrile]-iron(II) hexafluorophosphate (**3a**): (0·414 g, 79%) $\nu_{\max}(\text{cm}^{-1})$ (neat) 2320 (CN), 1335, 1165 (SO); $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3)$ 5·32 (5H, s, Cp), 6·46–6·70 (6H, m, complexed ArH and CH), 7·71–7·80 (2H, m, SO_2PhH), 7·85–7·99 (3H, m, SO_2PhH); $\delta_{\text{C}}(\text{CD}_3\text{COCD}_3)$ 61·96 (CH), 79·41 (5C, Cp), 87·68, 89·78, 89·82, 90·31, 91·47 (5C, ArC), 92·20 (quaternary ArC), 113·13 (CN), 130·81 (2C, SO_2PhC), 130·91 (2C, SO_2PhC), 137·29 (quaternary SO_2PhC).

(b) (η^5 -Cyclopentadienyl) [η^6 -(*o*-chlorophenyl)-phenylsulphonyl-acetonitrile]-iron(II) hexafluorophosphate (**3b**): (0·527 g, 94%) $\nu_{\max}(\text{cm}^{-1})$ (neat) 2300 (CN), 1338, 1163 (SO). $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3)$ 5·46 (5H, s, Cp), 6·71–7·08 (5H, s, complexed ArH and CH), 7·76–7·83 (2H, m, SO_2PhH), 7·93–8·02 (3H, m, SO_2PhH). $\delta_{\text{C}}(\text{CD}_3\text{COCD}_3)$ 60·25 (CH), 81·86 (5C, Cp), 89·40 (quaternary ArC), 88·10, 89·61, 90·96, 91·09 (4C, ArC), 109·50 (quaternary ArC), 113·41 (CN), 130·93 (2C, SO_2PhC), 131·23 (2C, SO_2PhC), 135·41 (quaternary SO_2PhC), and 137·63 (SO_2PhC).

(c) (η^5 -Cyclopentadienyl) [η^6 -(*m*-chlorophenyl)-phenylsulphonyl-acetonitrile]-iron(II) hexafluorophosphate (**3c**): (0·451 g, 81%) $\nu_{\max}(\text{cm}^{-1})$ (neat) 2280 (CN), 1345, 1162

(SO); $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3)$ 5.47 (5H, s, Cp), 6.40–7.06 (5H, m, complexed ArH and CH), 7.75–7.85 (2H, m, SO_2PhH), 7.90–8.05 (3H, m, SO_2PhH); $\delta_{\text{C}}(\text{CD}_3\text{COCD}_3)$ 61.38 (CH), 81.77 (5C, Cp), 86.57, 87.24, 89.61, 90.85 (4C, ArC), 92.95 (quaternary ArC), 108.44 (quaternary ArC), 112.71 (CN), 130.93 (4C, SO_2PhC), 135.17 (quaternary SO_2PhC), 137.40 (SO_2PhC).

(d) (η^5 -Cyclopentadienyl) [η^6 -(*p*-chlorophenyl)-phenylsulphonyl-acetonitrile]-iron(II) hexafluorophosphate (**3d**): (0.428 g, 77%) $\nu_{\text{max}}(\text{cm}^{-1})$ (neat) 2305 (CN), (1348, 1142 (SO); $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3)$ 5.44 (5H, s, Cp), 6.55–6.77 (3H, m, complexed ArH and CH), 7.02 (2H, d, $J = 6.2$, complexed ArH), 7.72–7.81 (2H, m, SO_2PhH), 7.89–7.98 (3H, m, SO_2PhH); $\delta_{\text{C}}(\text{CD}_3\text{COCD}_3)$ 61.12 (CH), 81.73 (5C, Cp), 87.40, 90.04, 90.07, 91.15 (4C, ArC), 91.51 (quaternary ArC), 109.09 (quaternary ArC), 112.93 (CN), 130.80 (2C, SO_2PhC), 130.91 (2C, SO_2PhC), 134.70 (quaternary SO_2PhC), and 137.32 (SO_2PhC).

4. Photolysis

1.0 mmol of complexes **2a–d**, **3a–d** were dissolved in a mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (30 ml:10 ml) in a pyrex tube. The solution was deoxygenated by bubbling nitrogen through it and the reaction tube was fitted into a photochemical apparatus equipped with a xenon lamp (lower limit = 290 nm), and irradiated at room temperature for 2 h. The solvent was concentrated to a volume of 1–2 ml using rotary evaporation, and introduced into a column of silica gel, prepared in hexane. The residue was washed with hexane, and the product eluted with chloroform by passage through a short column. Removal of the solvent from the eluate gave the expected liberated arene, with the following yields and spectral data.

(a) *Ethyl 2-phenyl cyanoacetate (4a)*: Yellowish crystals (0.151 g, 80%). $\nu_{\text{max}}(\text{cm}^{-1})$ (neat) 2220 (CN), 1750 (CO); $\delta_{\text{H}}(\text{CDCl}_3)$: 1.26 (3H, t, $J = 7.1$, CH_3), 4.23 (2H, q, $J = 7.2$, CH_2), 4.70 (1H, s, CH), 7.38–7.46 (5H, br s, ArH). $\delta_{\text{C}}(\text{CDCl}_3)$: 13.87 (CH_3), 43.76 (CH), 63.29 (CH_2), 115.60 (CN), 123.05 (quaternary ArC), 127.89, 129.20, 129.32 (5C, ArC), and 164.50 (CO). m/z 189 (M^+ , 3%), 145 (5), 117 (100), 89 (24).

(b) *Ethyl-(o-chlorophenyl) cyanoacetate (4b)*: (0.183 g, 82%), yellowish oil. $\nu_{\text{max}}(\text{cm}^{-1})$ (neat) 2220 (CN), 1750 (CO); $\delta_{\text{H}}(\text{CDCl}_3)$: 1.26 (3H, t, $J = 7.1$, CH_3), 4.23 (2H, q, $J = 7.2$, CH_2), 4.70 (1H, s, CH), 7.38–7.46 (5H, br s, ArH). $\delta_{\text{C}}(\text{CDCl}_3)$: 13.87 (CH_3), 43.76 (CH), 63.29 (CH_2), 115.60 (CN), 123.05 (quaternary ArC), 127.89, 129.20, 129.32 (5C, ArC), and 164.50 (CO). m/z 225 [^{37}Cl], 2], 223 [^{35}Cl], 5], 151 (100), 116 (20).

(c) *Ethyl-(m-chlorophenyl) cyanoacetate (4c)*: (0.187 g, 84%), yellowish oil. $\nu_{\text{max}}(\text{cm}^{-1})$ (neat) 2260 (CN), 1755 (CO); $\delta_{\text{H}}(\text{CDCl}_3)$: 1.27 (3H, t, $J = 7.0$, CH_3), 4.25 (2H, q, $J = 7.1$, CH_2), 4.67 (1H, s, CH), 7.35 (4H, br s, ArH). $\delta_{\text{C}}(\text{CDCl}_3)$: 13.82 (CH_3), 43.20 (CH), 63.56 (CH_2), 115.23 (CN), 126.08, 128.09, 129.48, 130.51 (4C, ArC), 131.59, 135.15 (quaternary ArC) and 164.34 (CO). m/z 225 [^{37}Cl], 4], 223 [^{35}Cl], 11], 151 (100), 116 (32).

(d) *Ethyl-(p-chlorophenyl) cyanoacetate (4d)*: (0.176 g, 79%), yellowish oil. $\nu_{\text{max}}(\text{cm}^{-1})$ (neat) 2300 (CN), 1750 (CO); $\delta_{\text{H}}(\text{CDCl}_3)$: 1.26 (3H, t, $J = 7.1$, CH_3), 4.23 (2H, q, $J = 7.1$, CH_2), 4.68 (1H, s, CH), 7.39 (4H, br s, ArH). $\delta_{\text{C}}(\text{CDCl}_3)$: 13.82 (CH_3), 43.05 (CH), 63.49 (CH_2), 115.22 (CN), 128.37 (quaternary ArC), 129.25, 129.49 (4C, ArC), 135.40 (quaternary ArC) and 164.52 (CO). m/z 225 [^{37}Cl], 3], 223 [^{35}Cl], 10], 151 (97), 116 (15).

(e) *Phenyl phenylsulphonylacetonitrile (5a)*: Yellowish solid (0.206 g, 80%). $\nu_{\text{max}}(\text{cm}^{-1})$ (neat) 2310 (CN), 1370, 1160 (SO). $\delta_{\text{H}}(\text{CDCl}_3)$: 5.15 (1H, s, CH), and 7.25–7.74 (10H

m, 2 Ph). $\delta_{\text{C}}(\text{CDCl}_3)$: 63.00 (CH), 113.37 (CN), 125.34 (quaternary ArC), 128.98 (2C, SO_2PhC), 129.14 (2C, SO_2PhC), 129.68 (2C, ArC), 130.01 (2C, ArC), 130.45 (1C, ArC), 134.29 (quaternary SO_2PhC), and 135.19 (SO_2PhC). m/z 257 (M^+ , 15%), 141 (16), 116 (100), 77 (26).

(f) (*o*-Chlorophenyl)phenylsulphonylacetonitrile (**5b**): White solid (0.215 g, 74%). $\nu_{\text{max}}(\text{cm}^{-1})$ (neat) 2305 (CN), 1340, 1165 (SO). $\delta_{\text{H}}(\text{CDCl}_3)$: 5.81 (1H, s, CH), 7.34–7.63 (4H, *m*, ArH), 7.74–7.85 (2H, *m*, SO_2PhH), 7.84–7.89 (3H, *m*, SO_2PhH). $\delta_{\text{C}}(\text{CDCl}_3)$: 58.94 (CH), 113.26 (CN), 124.08 (quaternary ArC), 127.70 (ArC), 129.50 (2C, SO_2PhC), 130.00 (2C, SO_2PhC), 130.19, 131.26, and 132.04 (3C, ArC), 135.30 (quaternary SO_2PhC), 135.45 (SO_2PhC), 135.60 (quaternary ArC). m/z 293 [^{37}Cl], 8], 291 [^{35}Cl], 20], 150 (100), 77 (74).

(g) (*m*-Chlorophenyl)phenylsulphonylacetonitrile (**5c**): Yellowish oil (0.204 g, 70%). $\nu_{\text{max}}(\text{cm}^{-1})$ (neat) 2305 (CN) and 1340, 1162 (SO). $\delta_{\text{H}}(\text{CDCl}_3)$: 5.12 (1H, s, CH) and 7.18–7.46 (4H, *m*, ArH), 7.52–7.62 (2H, *m*, SO_2PhH), 7.72–7.80 (3H, *m*, SO_2PhH). $\delta_{\text{C}}(\text{CDCl}_3)$: 62.16 (CH), 112.90 (CN), 127.09 (quaternary ArC), 127.82 (ArC), 129.22 (2C, SO_2PhC), 129.62 (ArC), 129.87 (2C, SO_2PhC), 130.14, 130.60 (2C, ArC), 133.99 (quaternary SO_2PhC), 134.84 (quaternary ArC), and 135.40 (SO_2PhC). m/z 293 [^{37}Cl], 4], 291 [^{35}Cl], 14], 141 (91), 77 (100).

(h) (*p*-Chlorophenyl)phenylsulphonylacetonitrile (**5d**): Yellowish oil (0.218 g, 75%). $\nu_{\text{max}}(\text{cm}^{-1})$ (neat) 2305 (CN) and 1338, 1160 (SO). $\delta_{\text{H}}(\text{CDCl}_3)$: 5.12 (1H, s, CH), and 7.21 (2H, *d*, $J = 8.4$, ArH), 7.34 (2H, *d*, $J = 8.4$, ArH), 7.51–7.65 (2H, *m*, SO_2PhH), 7.75–7.81 (3H, *m*, SO_2PhH). $\delta_{\text{C}}(\text{CDCl}_3)$: 60.08 (CH), 113.07 (CN), 123.82 (quaternary ArC), 129.25 (4C, SO_2PhC), 129.91, 130.94 (4C, ArC), 134.13 (quaternary SO_2PhC), 135.35 (SO_2PhC), and 136.90 (quaternary ArC). m/z 293 [^{37}Cl], 3], 291 [^{35}Cl], 7], 150 (100), 141 (11), 77 (28).

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