One-Pot Syntheses of Methyl *p*- and *o*-Hydroxydithiobenzoates from Phenol Ethers

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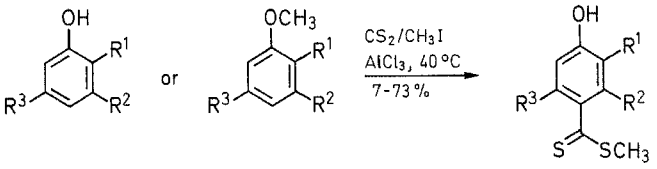
Methyl *p*- and *o*-hydroxydithiobenzoates were prepared regiospecifically in a one-pot procedure from phenol methyl- and methoxymethyl, ethers, respectively. The *p*-hydroxy compounds were prepared by treatment of the methyl ethers with carbon disulfide, methyl iodide, and aluminum chloride. The second procedure involves ortho-metallation, carbon disulfide dithiocarboxylation, sulfur alkylation with methyl iodide, and *in situ* phenol deprotection with aluminum chloride/methyl iodide.

In the course of our studies on the chemistry of acylketene dithioacetals,[1] we required regiospecific syntheses of hydroxydithiobenzoates as potential intermediates for the preparation of quinone methide acyl- or 3-oxoalkylketene dithioacetals. Surprisingly few reports have appeared describing the preparation of hydroxydithiobenzoates.[2-4] Although these compounds have been[2] prepared by treatment of phenols and naphthols with base, carbon disulfide, and an alkylating reagent, the regiochemistry and yields obtained were highly substrate dependent. Excellent yields were obtained for resorcinol (88%) and 2,6-di-*tert*-butylphenol (96%), but decreased significantly for simple naphthols (30–60%) and 2,6-diisopropylphenol (63%). In our hands, the procedure did not work for simple and moderately substituted benzene derivatives. In an effort to obtain hydroxydithiobenzoates we explored Friedel-Crafts dithiocarboxylation procedures employing carbon disulfide. Although the reaction of phenol ethers with carbon disulfide and aluminum chloride was first reported[5] in 1927, the procedure reproducibly[6] afforded dithio esters in yields of only 1–5%. It is interesting to note that carbon disulfide is often used as a solvent in Friedel-Crafts reactions and low yields of aromatic sulfur compounds have been detected.[7]

A recent report[8] on the regiospecific *ortho*-acylation of phenols prompted a similar search for regiocontrol in the Friedel-Crafts dithiocarboxylation reaction employing carbon disulfide. In contrast to the acylation reactions, carbon disulfide dithiocarboxylation uniformly afforded the *para*-substituted derivatives and a report[9] on the preparation of dithiosalicyclic acid appears to be incorrect. All attempts to exploit the phenol hydroxyl group as a directing substituent in the Friedel-Crafts dithiocarboxylation reaction via aluminum and boron[8] phenoxide intermediates were unsuccessful. Similarly, magnesium[10] and copper phenoxides, respectively, afforded the *para*-substituted derivatives in low yields or did not undergo dithiocarboxylation with carbon disulfide. Since *o*-hydroxybenzoates could be potentially prepared by Friedel-Crafts carboxylation procedures,[8,11] the use of various sulfur transfer reagents was examined. Although thioamides[12] are readily prepared from aryl amides by use of Lawesson's reagent,[13] similar procedures proved unsuccessful for the *o*-hydroxybenzoic acids or benzoates. Usually, mixtures of thio- and dithiobenzoic acids and benzoates were obtained in low yields. The yields of sulfur compounds could not be improved by the use of ultrasound[12,14] or high pressure reaction conditions. With these approaches for regioselective control thwarted, the use of *ortho*-metalation[15,16] procedures was examined.

Friedel-Crafts dithiocarboxylation can, in principle, be effected on either the free or protected phenol. In the initial studies, phenols **1a–h** (Scheme A) were treated with carbon disulfide, methyl iodide, and aluminum chloride. Variation in the time, temperature, and equivalents of aluminum chloride afforded slight improvement in the yields of *p*-hydroxydithiobenzoates **3a–h**, which ranged from 7–40% (Table 1, entries 1, 5, 7, 9, 11, and 13). The use of ultrasound or high-pressure reaction conditions did not significantly increase the yields.



1 **2** **3**

1–3	R^1	R^2	R^3	1–3	R^1	R^2	R^3
a	H	H	H	**e**	H	OH **(1, 3)**	H
b	Cl	H	H		H	OCH_3 **(2)**	H
c	Br	H	H	**f**	CH_3	H	CH_3
d	H	CH_3	H	**g**	$-(CH_2)_4-$		H
				h	$-(CH=CH)_2-$		H

Scheme A

The low yields obtained in these phenol Friedel-Crafts dithiocarboxylations forced us to examine a two-step strategy employing phenol protecting groups (Scheme A). Treatment of methoxybenzene **(2a)** under comparable conditions afforded methyl *p*-hydroxydithiobenzoate **(3a)** in 73% yield (Table 1, entry 2). Material balance was largely accounted for by recovered methoxybenzene (16–18%) and the yield of dithioester could not be increased by using longer reaction times, higher temperatures, or additional quantities of aluminum chloride. Use of smaller quantities of aluminum chloride (0.5 equiv) afforded low yields (11–13%) of dithioesters even when the reaction mixture was stirred overnight. The reaction afforded a very clean thin layer chromatogram and the *o*-dithio ester was not observed.[17] Clean formation of the *p*-hydroxydithiobenzoate coupled with the substantial recovery of unreacted methoxybenzene strongly suggests that ether cleavage occurs after dithiocarboxylation. Similarly, good yields of dithiobenzoates could be obtained from a variety of alkyl substituted phenol methyl esters **2d, 2f–g**, and 1-methoxynaphthalene **(2h)** (Table 1, entries 6, 10, 12, and 14), which were either commercially available or readily prepared from the phenols.[18] Good yields of dithioesters could not be obtained from phenol methyl ethers containing additional heteroatoms such as chloro- **2b** (entry 3), bromo- **2c** (entry 4), or alkoxy substituents **2e** (entry 8). 2-Bromomethoxybenzene **(2c)**, however, afforded significantly higher yields of dithioester than the corresponding 2-chloro analog. These results probably reflect diminished aromatic reactivity resulting from the deactivating nature of the substituent or from complexation of the substituent with the Lewis acid. Deactivation of 1,3-dimethoxybenzene **(2e)** via complexation with aluminum chloride is consistent with the observation that the dithioesters could not be obtained from phenol methoxymethyl ethers.

It is also interesting to note that *p*-substituted phenol ethers **4a–b** yielded *o*-hydroxydithiobenzoates **5a–b** in low yields under these reaction conditions (Scheme B). 4-Methylmethoxybenzene **(4a)** gave recovered starting material (51%),

Table 1. Methyl *p*-Hydroxydithiobenzoates **3a–h** Prepared

Entry	Product	Method[a]	Yield[b] (%)	Molecular Formula[c] or Lit. mp (°C)	IR (CCl_4) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)	MS m/z (%)
1	**3a**	A	37–40	–[d]	3400, 2980, 1605, 1510, 1480, 1380, 1240, 1180, 1052	2.79 (s, 3H); 5.89 (br s, 1H); 6.85 (d, 2H, J = 8); 8.1 (d, 2H, J = 8)	65 (7); 137 (100); 138 (7); 184 (25)
2		B	73				
3	**3b**	B	25	$C_8H_7ClOS_2$ (218.7)	3400, 1600, 1480, 1450, 1400, 1290, 1250, 1180, 1120, 1050	2.77 (s, 3H); 5.95 (br s, 1H); 6.99 (d, 1H, J = 8); 7.86–8.02 (m, 1H); 8.13 (d, 1H, J = 3)	63 (5); 107 (7); 171 (100); 172 (5); 173 (3); 218 (42); 220 (14)
4	**3c**	B	39	$C_8H_7BrOS_2$ (263.3)	3400, 1605, 1475, 1440, 1400, 1280, 1250, 1170, 1120, 1050	2.8 (s, 3H); 6.00 (br s, 1H); 7.1 (d, 1H, J = 8); 7.9–8.1 (m, 1H); 8.2 (d, 1H, J = 3)	63 (7); 171 (8); 173 (7); 199 (95); 201 (100); 215 (11); 217 (12); 246 (7); 248 (8); 262 (5); 263 (1); 264 (5)
5	**3d**	A	17	$C_9H_{10}OS_2$ (198.3)	3400, 2905, 1600, 1570, 1490, 1440, 1290, 1250, 1160, 1110, 1050	2.32 (s, 3H); 2.75 (s, 3H); 5.37 (br s, 1H); 6.52–6.66 (m, 2H); 7.15 (d, 1H, J = 8.5)	121 (8); 133 (9); 151 (100); 183 (74); 198 (30)
6		B	70				
7	**3e**	A	7–10	96[2]	3300, 3400, 1610, 1550, 1380, 1300, 1240, 1170, 1150, 1070, 1050	2.72 (s, 3H); 5.80 (br s, 1H); 6.34–6.52 (m, 2H); 8.1 (d, 1H, J = 9); 12.01 (s, 1H)	65 (5); 153 (100); 181 (5); 182 (15); 200 (40); 202 (12)
8		B	15–17				
9	**3f**	A	30	$C_{10}H_{12}OS_2$ (212.3)	3400, 2920, 1610, 1580, 1480, 1400, 1260, 1210, 1115, 1040	2.18 (s, 3H); 2.29 (s, 3H); 2.73 (s, 3H); 5.09 (br s, 1H); 6.58 (s, 1H); 7.04 (s, 1H)	77 (9); 91 (13); 121 (16); 135 (11); 149 (25); 150 (42); 164 (14); 165 (100); 166 (10); 195 (66); 212 (32)
10		B	72				
11	**3g**	A	31	$C_{12}H_{14}OS_2$ (238.4)	3400, 2920, 1585, 1440, 1305, 1230, 1170, 1100, 1050	1.78 (m, 4H); 2.72 (m, 7H); 5.15 (s, 1H); 6.51–7.24 (m, 2H)	91 (8); 115 (8); 128 (7); 135 (8); 147 (7); 163 (14); 189 (8); 190 (9); 191 (9); 223 (100); 223 (10); 225 (8); 238 (8)
12		B	69				
13	**3h**	A	27	113–114[4]	3300, 2920, 1590, 1575, 1510, 1455, 1350, 1230, 1170, 1100, 1050	2.84 (s, 3H); 6.10 (br s, 1H); 6.66 (d, 1H, J = 8); 7.24–7.77 (m, 3H); 8.04–8.49 (m, 2H)	114 (18); 115 (82); 158 (34); 186 (90); 187 (100); 188 (12); 234 (74)
14		B	68				

[a] A = Phenol (1.0 equiv), CS_2 (2.5 equiv), CH_3I (2.0 equiv) $AlCl_3$ (1.5 equiv), 40 °C, 20–30 min.
B = Aryl ether (1.0 equiv), CS_2 (4.0 equiv), CH_3I (2.0 equiv), $AlCl_3$ (1.5 equiv) added over 1 h at 40 °C, 40 °C for 20–30 min. after addition of $AlCl_3$.

[b] Yields are based upon isolated products purified by either MPLC or preparative TLC.

[c] Satisfactory microanalyses obtained: C ±0.19, H ±0.10; exception **3b** and **3c**.

[d] Not reported in the original literature.[6]

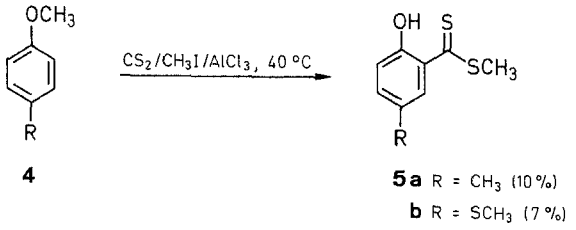
Table 2. Methyl *o*-Hydroxydithiobenzoates **8a–g** Prepared

Product	Yield[a] (%)	Molecular Formula[b] or Lit. mp (°C)	IR (CCl_4) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)	MS m/z (%)
8a	65	$C_8H_8OS_2$ (184.3)	3430, 2960, 1610, 1560, 1460, 1270, 1200, 1150, 1050, 920	2.73 (s, 3H); 6.87–8.19 (m, 4H); 12.51 (s, 1H)	45 (20); 65 (18); 109 (13); 137 (100); 184 (19)
8b	68	$C_9H_{10}OS_2$ (198.3)	3380, 2900, 1610, 1565, 1485, 1270, 1200, 1050, 925	2.33 (s, 3H); 2.72 (s, 3H); 6.92–7.94 (m, 3H); 11.98 (s, 1H)	121 (7); 151 (100); 152 (5); 198 (50)
8c	70	$C_9H_{10}OS_3$ (230.4)	3380, 2950, 1608, 1570, 1465, 1290, 1200, 1060, 925	2.48 (s, 3H); 2.74 (s, 3H); 6.97–8.08 (m, 3H); 12.01 (s, 1H)	45 (15); 168 (251); 182 (48); 183 (87); 230 (100)
8d	60	$C_9H_{10}OS_2$ (198.3)	3360, 2920, 1610, 1560, 1480, 1270, 1200, 1150, 1055, 930	2.29 (s, 3H); 2.70 (s, 3H); 6.69–8.04 (m, 3H); 12.32 (s, 1H)	77 (8); 121 (8); 151 (100); 152 (5); 198 (38)
8e	53	$C_9H_{10}OS_2$ (198.3)	3380, 2930, 1610, 1570, 1485, 1270, 1200, 1150, 1050, 925	2.28 (s, 3H); 2.70 (s, 3H); 6.69–8.04 (m, 3H); 12.39 (s, 1H)	77 (5); 121 (8); 151 (100); 152 (6); 198 (51)
8f	68	–[4]	3400, 2960, 1610, 1560, 1450, 1270, 1205, 1150, 1050, 920	2.75 (s, 3H); 7.19–7.74 (m, 4H); 8.14 (d, 1H, J = 8); 8.5 (d, 1H, J = 8); 12.65 (s, 1H)	115 (28); 158 (11); 186 (29); 187 (100); 234 (56)
8g	40–45	$C_{12}H_{14}OS_2$ (238.4)	3380, 2920, 2840, 1585, 1450, 1270, 1200, 1140, 1040, 970	1.74 (m, 4H); 2.73 (m, 7H); 6.70–7.3 (m, 2H); 12.42 (s, 1H)	115 (7); 128 (8); 135 (7); 163 (162); 191 (9); 223 (100); 224 (11); 225 (9); 238 (44)

[a] Yields are based upon isolated products purified by preparative TLC.

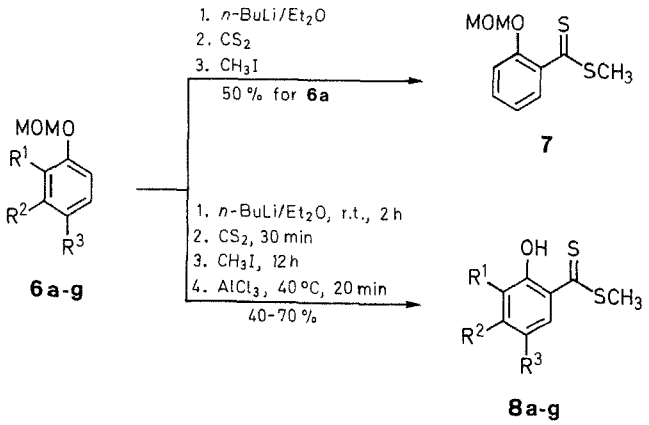
[b] Satisfactory microanalyses were obtained: (C ±0.38, H ±0.16), except for **8e** which gave satisfactory mass spectral data.

dithioester **5a** (10%), and 4-methylphenol (7%) in addition to uncharacterized material at the origin of the thin layer chromatography plate. Attempts to make the corresponding dithioic acids were unsuccessful and this is consistent with the reported instability of dithiotic acids under Friedel-Crafts reaction conditions.[7] The use of chlorotrimethylsilane did not afford trimethylsilyl protected dithioic acids.



Scheme **B**

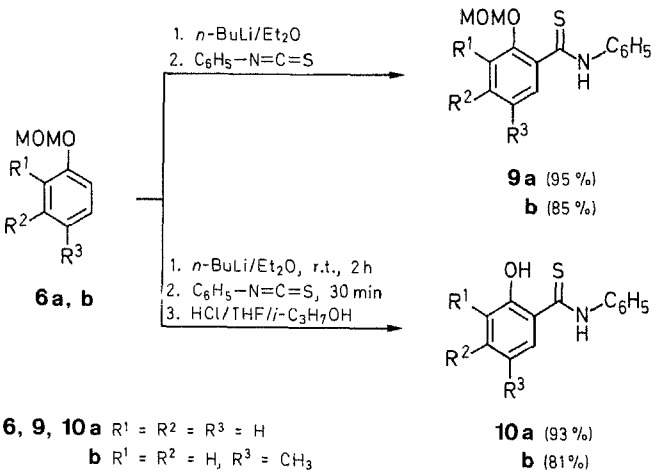
The use of phenol methoxymethyl ethers, readily prepared in 80–90% yield by an established procedure,[19] was explored in an *ortho*-metalation procedure[15] (Scheme **C**). In the initial experiment, phenol ether **6a** was treated with *n*-butyllithium, quenched with carbon disulfide, and then treated with methyl iodide. Work-up of the crude reaction mixture afforded the aryl dithioester **(7)** with the methoxymethyl protecting group intact in 60% yield. The formation of lithium iodide in the reaction mixture suggested a possible *in situ* deprotection involving the addition of aluminum chloride since an aluminum halide ethanethiol combination effectively cleaves methyl ethers.[20] This was indeed the case, and methyl *o*-hydroxydithiobenzoate **(8a)** could be isolated in 65% yield (Table 2). The procedure was readily extended to substituted phenol ethers **6b–g** and the corresponding *o*-hydroxydithiobenzoates **8b–g** could be isolated in yields of 40–70% (Table 2). The dianion derived from phenol[21] could not be prepared in tetrahydrofuran because reaction with the solvent is faster than *ortho*-lithiation and this strategy was not examined further.



6, 8	R^1	R^2	R^3	6, 8	R^1	R^2	R^3
a	H	H	H	**e**	CH_3	H	H
b	H	H	CH_3	**f**	$-(CH=CH)_2-$		H
c	H	H	SCH_3	**g**	$-(CH_2)_4-$		H
d	H	CH_3	H				

Scheme **C**

The *ortho*-metalated intermediate could also be trapped with phenyl isothiocyanate to afford the hydroxy protected thioamide **9a** ($R^1=R^2=R^3=H$, 95%) in excellent yield (Scheme **D**). Cleavage of the methoxymethyl ether functionally could be effected with aluminum chloride/sodium iodide, although the reaction did not generally go to completion after 1 h at 40 °C (at which time substantial material began to appear at the origin of thin layer chromatograms). Alternatively, treatment of the crude reaction solution with concentrated hydrochloric acid in tetrahydrofuran/isopropyl alcohol at room temperature for 12 h (overnight) gave the *ortho*-hydroxythioamides **10a–b** in excellent yields in a one pot procedure.



Scheme **D**

In summary, methyl *p*-hydroxydithiobenzoates can be prepared in a single pot process from phenol methyl ethers, methyl iodide, and anhydrous aluminum chloride in carbon disulfide. The reaction is clean, regiospecific, and affords the phenols directly by *in situ* cleavage of the product phenol methyl ethers under the reaction conditions. The regiospecific functionalization of phenols remains a difficult operation and the present method should be contrasted with the boron trichloride catalyzed *ortho*-acylation of phenols.[8] The procedure affords dithioesters in good yields from alkyl substituted phenol ethers and in poor yields from aryl ethers containing additional heteroatom substituents.

o-Hydroxy dithiobenzoates and thiobenzamides can be prepared in a one pot process from phenol methoxymethyl ethers in good overall yields. The reactions are clean, regiospecific, and afford the phenols directly by *in situ* cleavage of the phenol methoxymethyl ethers upon addition of anhydrous aluminum chloride or concentrated hydrochloric acid.

IR spectra were recorded on a Perkin-Elmer 1310 spectrometer and ^{1}H-NMR spectra were measured on a JEOL FX-90Q spectrometer. Mass spectral data were obtained on a Hewlett-Packard mass spectrometer (5985B). NH_4Cl and CS_2 were obtained commercially and used without further purification. Ether is distilled from sodium/benzophenone prior to use.

Methyl *p*-Hydroxydithiobenzoates 3a–h; General Procedures:

Method A, (for **3a–h**): The procedure is identical to that described in Method B except that phenols **1a–h** are used.

Method B, (for **3a–h**): The phenol methyl ether **2a–h** (10 mmol), CS_2 (2.28 g, 30 mmol), and MeI (2.84 g, 20 mmol) are mixed together in a round bottom flask and heated to 40 °C. Anhydrous $AlCl_3$ (2.0 g, 15 mmol) is added to this mixture as a solid over a period of 1 h. Rapid addition of anhydrous $AlCl_3$ in a single batch results in low yields of dithioesters. The mixture is stirred for an additional 30 min. at 40 °C, cooled to room temperature, and diluted by the dropwise addition of water (Caution!) since this is highly exothermic. The product is ex-

tracted with CH_2Cl_2 (3 × 30 mL). The combined CH_2Cl_2 extract is washed with brine (3 × 25 mL), dried ($MgSO_4$), and concentrated *in vacuo* to afford the crude dithioesters **3a–h** which are purified by column chromatography on silica gel (60–230 mesh, Davison). Initial elution with petroleum ether affords unreacted phenol methyl ethers whereupon elution with petroleum ether/5% EtOAc affords pure dithioesters (Table 1).

Methyl *o*-Hydroxydithiobenzoates 5a, b from *p*-Substituted Phenol Ethers 4a, b; General Procedure:
The procedure is identical to that described for the preparation of **3a–h**. For analytical and spectroscopical data see Table 2, compounds **8b** and **8c**, which are identical to **5a** and **5b**.

Methyl 2-Methoxymethyldithiobenzoate (7):
The procedure is identical to that described for the preparation of **8a–g** except that $AlCl_3$ is not added to the reaction mixture. The mixture is stirred for 8 h after addition of MeI and then diluted with H_2O and extracted with ether (2 × 10 mL). The ether extracts are washed with H_2O (1 × 10 mL), brine (1 × 10 mL), dried ($MgSO_4$), and concentrated *in vacuo*. Purification by preparative TLC (Silica gel, 2000 μ, petroleum ether/5% EtOAc, R_f 0.48) affords 160 mg of **7** from 162 mg (1.17 mmol) of **6a**; yield: 60%.

IR (Neat): 2955, 2920, 1590, 1480, 1448, 1225, 1195, 1150, 1113, 1062, 985, 920, 883, 750 cm^{-1}.

NMR ($CDCl_3$/TMS): δ = 2.75 (s, 3H); 3.46 (s, 3H); 5.18 (s, 2H); 6.94–7.41 (m, 4H).

Methyl *o*-Hydroxydithiobenzoates 8a–g; General Procedure:
The phenol methoxymethyl ether **6a–g** (1 mmol) in dry ether (5 mL) under a N_2 atmosphere is treated with a 2.2 M hexane solution of *n*-BuLi (0.6 mL, 1.3 mmol) and the mixture is stirred at room temperature for 2 h to give a cloudy white suspension. CS_2 (2 mL) is added, whereupon an orange suspension forms, and the mixture is stirred for 30 min. Addition of MeI (0.25 mL, 3.9 mmol) results in the formation of a clear reddish orange solution which is stirred overnight (12 h) and then treated with anhydrous $AlCl_3$ (15 mg), heated to 40 °C, and stirred for 20 min. The solution is cooled to room temperature, slowly quenched with water and diluted with ether. The aqueous phase is extracted with ether (2 × 20 mL), the combined organic phase is washed with brine (2 × 20 mL), dried ($MgSO_4$), and concentrated *in vacuo*. Purification by preparative TLC (silica gel, 1000 μ, petroleum ether 5% EtOAc) affords pure dithioesters **8a–g** (Table 2).

2-Methoxymethylthiobenzanilides 9a, b; General Procedure:
The procedure is identical to that described for the preparation of **10a–b** except that conc. HCl in THF/isopropyl alcohol is not added. The reaction is worked up 0.5 h after addition of phenyl isothiocyanate by dilution with H_2O (10 mL) and ether extraction (2 × 25 mL). The combined organic phase is washed with H_2O (2 × 10 mL), brine (2 × 10 mL), dried ($MgSO_4$) and concentrated *in vacuo*.

9a: NMR ($CDCl_3$/TMS): δ = 3.53 (s, 3H); 5.36 (s, 2H); 6.97–7.64 (m, 6H); 7.73–7.95 (m, 2H); 8.35 (d, J = 8.0 Hz, 1H); 10.39 (br s, 1H).

9b: NMR ($CDCl_3$/TMS): δ = 2.35 (s, 3H); 3.52 (s, 3H); 5.30 (s, 2H); 6.92–7.68 (m, 5H); 7.68–7.63 (m, 2H); 9.26 (br s, 1H); 10.45 (br s, 1H).

2-Hydroxythiobenzanilides 10a–b; General Procedures:
The phenol methoxymethyl ether (**1a** or **1b**, 1 mmol) and dry ether (5 mL) is added to a 25 mL round bottomed flask under nitrogen. A 2.2 M hexane solution of *n*-BuLi (0.6 mL, 2.2 M, 1.3 mmol) is added via syringe and stirring is continued at room temperature for 2 h whereupon a cloudy suspension is formed. CS_2 (2.0 mL) is added to give an orange suspension and the mixture is stirred for 0.5 h. Phenylisothiocyanate (0.2 mL) is added at room temperature and the mixture is stirred for an additional 0.5 h. The mixture is then treated with conc. HCl (0.25 mL) in THF (1 mL/isopropyl alcohol (2 mL) and stirred for 12 h (overnight) at room temperature. The solution is diluted with water (10 mL) and extracted with ether (2 × 25 mL). The combined organic phase is washed with 5% $NaHCO_3$ (2 × 20 mL), water (2 × 20 mL), and brine (2 × 20 mL), dried ($MgSO_4$), and concentrated *in vacuo*. Purification by column chromatography (silica gel, 60–230 mesh, Davison, petroleum ether/5% EtOAc) gives pure *o*-hydroxythiobenzanilides **10a–b.**[22]

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