quantities of solvent and reactants were used: cyclododecanol (10 mmol), *sec*-phenethyl alcohol (10 mmol), Me_2SO (24 mmol), TFAA (22 mmol), TEA (8 ml), and CH_2Cl_2 (ca. 100 ml). GLC of the reaction mixture showed that the products consisted of *sec*-phenethyl trifluoroacetate (97%), acetophenone (0%), cyclododecyl trifluoroacetate (5%), and cyclododecanone (84%). The reaction mixture was concentrated to ca. 40 ml under vacuum at room temperature, and excess 0.1 M 2,4-D-solution (120 ml) was added. A yellow precipitate of cyclododecanone 2,4-D, mp 148–149.5 °C (lit.[9] 152–153 °C), was obtained (85%).

B. Equimolar Mixture of 1-Decanol and 2-Cyclohexenol (Procedure C). The reaction was carried out according to procedure C as in A above except that the following quantities of solvent and reactants were used: 1-decanol (10 mmol), 2-cyclohexenol (10 mmol), Me_2SO (24 mmol), TFAA (21 mmol), TEA (8 ml), and CH_2Cl_2 (ca. 105 ml). GLC analysis of the reaction mixture showed that the products consisted of 2-cyclohexenyl trifluoroacetate (97%), 2-cyclohexenone (0%), *n*-decyl trifluoroacetate (26%), and 1-decanal (61%). The reaction mixture was concentrated to ca. 30 ml, and excess 0.1 M 2,4-D (120 ml) was added to the concentrate. Yellow crystals of 1-decanal 2,4-D, mp 99–101 °C (lit.[7] 104 °C), were obtained (61%).

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Registry No.—Ib, 407-25-0; IIb, 57738-66-6; IVb, 57738-67-7; V (R′ = H; R″ = C_9H_{19}), 57738-68-8; V (R′ = H; R″ = Ph-CH_2), 57738-69-9; V (R′, R″ = $-(CH_2)_5-$), 19182-88-8; V (R′ = CH_3; R″ = C_6H_{13}), 57738-70-2; Me_2SO, 67-68-5; TEA, 121-44-8.

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(18) Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Ir spectra were obtained as liquid films using a Pye Unicam SP 1000 infrared spectrophotometer. NMR spectra were obtained with a Varian A-60A spectrometer, using CCl_4 as solvent and Me_4Si as internal standard. Gas chromatographic analyses were performed on a Wilkens Aerograph Model A-700 using a 12 ft × 0.25 in. column packed with 20% dilauryl phthalate on Chromosorb P or a 10 ft × 0.25 in. column packed with 20% SE-30 on Chromosorb W with He as carrier gas. Me_2SO was distilled from calcium hydride under atmospheric pressure, and the heart cut was stored over Linde molecular sieve, Type 3A, in a brown bottle sealed with a serum cap. TFAA, containing ca. 0.1% of TFA as an impurity, was used as purchased. Triethylamine (TEA) was stored over NaOH pellets overnight, then distilled and stored over Linde molecular sieve, Type 3A, in a sealed bottle. Methylene chloride was distilled from phosphorus pentoxide and kept over Linde molecular sieve, Type 3A, in a sealed bottle. Cyclohexenol, 3-butyn-2-ol, and allyl alcohol were distilled under nitrogen before use. Other alcohols were used as received; their purity was >96%.
(19) **Note Added in Proof.** Benzoin yields benzil (88%, procedure A), ethyl lactate yields ethyl pyruvate (70%, A; 78%, C), and 2-chlorocyclohexane yields 2-chlorocyclohexanone (67%, A; 63%, C).

Friedel–Crafts Thioacylation with Ethoxycarbonyl Isothiocyanate. A One-Step Synthesis of Aromatic Thioamides

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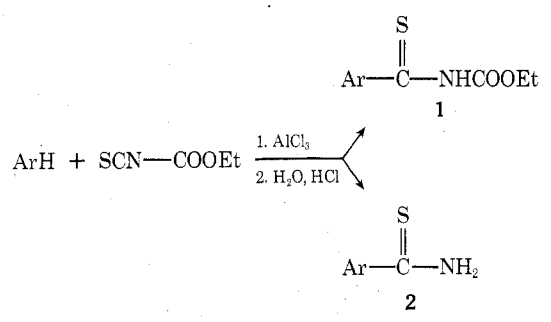
The aluminum chloride catalyzed reaction of ethoxycarbonyl isothiocyanate with aromatic compounds yields *N*-ethoxycarbonylthioamides when equimolar amounts of the two reagents are allowed to react in dichloromethane at 0–3 °C. The same reaction, however, leads directly to the corresponding thioamides when run in an excess of the aromatic compound as solvent, at room or higher temperature.

In the course of an investigation of cyclization reactions of *N*-ethoxycarbonylthioamides, the need arose for a method of preparation of such derivatives of aromatic thioamides. A Friedel–Crafts thioacylation using ethoxycarbonyl isothiocyanate appeared to be the most straightforward approach to these compounds, in view of the known, aluminum chloride catalyzed reactions of isocyanates[1] and isothiocyanates[2] with aromatic compounds.

As anticipated, it has been found that ethoxycarbonyl isothiocyanate reacts readily with various aromatic compounds in the presence of anhydrous aluminum chloride. However, depending upon the conditions, the reaction yields either the expected *N*-ethoxycarbonylthioamide (1), or the thioamide itself (2). The latter result is closely analogous to the formation of benzamide when benzene reacts with chlorosulfonyl isocyanate in the presence of $AlCl_3$.[3] Typically, the reaction of equimolar quantities of reagents,



dissolved in CH_2Cl_2, run in the presence of 1.5 or 2.0 molar equiv of $AlCl_3$, at 0–3 °C, yields the original adduct 1. On the other hand, when a large excess of the aromatic reagent is used as solvent and the reaction is run with 2.0 or more mol of $AlCl_3$ at ambient or higher temperature, addition of

Table I[a]

S
‖
Ar—C—NHCOOEt

					Ir, cm^{-1}		NMR, ppm			
1	Ar	Method	% yield[b]	Mp, °C	NH	CO	NH	Aromatic ring	R[c]	COOEt
a	C_6H_5	A	52	61–62.5[d]	3200	1760	12.0 (s, 1)	7.1–7.6 (m, 5)		4.1 (q, 2), 1.2 (t, 3)
b	4-MeC_6H_4	A	63	98–100	3200	1760	11.8 (s, 1)	7.4 (m, 2), 7.0 (m, 2)	2.3 (s, 3)	4.1 (q, 2), 1.2 (t, 3)
c	4-EtC_6H_4	A	67	60–62	3290, 3250	1740	11.8 (s, 1)	7.4 (m, 2), 7.0 (m, 2)	2.5 (q, 2), 1.1 (t, 3)	4.1 (q, 2), 1.2 (t, 3)
d	4-*i*-Pr-C_6H_4	A	60	70–72	3270	1740	11.9 (s, 1)	7.4 (m, 2), 7.1 (m, 2)	2.8 (m, 1), 1.2 (d, 6)	4.1 (q, 2), 1.2 (t, 3)
e	4-*t*-Bu-C_6H_4	A	41	111–113	3230	1740	11.8 (s, 1)	7.4 (m, 2), 7.1 (m, 2)	1.3 (s, 9)	4.0 (q, 2), 1.2 (t, 3)
f	2,5-DiMe-C_6H_3	B	84	66–68	3170	1770	12.2 (s, 1)	6.7 (m, 3)	2.2 (s, 3), 2.1 (s, 3)	4.1 (q, 2), 1.1 (t, 3)
g	2,4,6-Tri-MeC_6H_2	B	78	87–88	3250	1730	12.3 (s, 1)	6.6 (s, 2)	2.2 (s, 3), 2.1 (s, 6)	3.9 (q, 2), 1.1 (t, 3)
h	4-MeO-C_6H_4	C	90	88–90	3180	1750	11.7 (s, 1)	7.5 (m, 2), 6.7 (m, 2)	3.7 (s, 3)	4.1 (q, 2), 1.2 (t, 3)
i	4-EtO-C_6H_4	C	90	91–92.5	3190	1750	11.7 (s, 1)	7.6 (m, 2), 6.8 (m, 2)	4.0 (q, 2), 1.3 (t, 3)	4.2 (q, 2), 1.3 (t, 3)
j	4-ClC_6H_4	D	29	117–118	3180	1750	12.1 (s, 1)	7.5 (m, 2), 7.2 (m, 2)		4.1 (q, 2), 1.2 (t, 3)
k	4-BrC_6H_4	E	17	130–131.5	3180	1750	12.1 (s, 1)	7.4 (s, 4)		4.1 (q, 2), 1.2 (t, 3)

[a] Satisfactory analytical data (±0.3% for C, H, N) were reported for all new compounds listed in this table. [b] Crude or partially purified product with melting point lower than that of the analytical sample by 2–10 °C. [c] Alkyl or alkoxy substituent(s) attached to the aromatic ring. [d] Lit. mp 63 °C: J. Goerdeler and H. Schenk, *Chem. Ber.*, **44**, 782 (1966).

ice and hydrochloric acid at the end of the reaction period causes vigorous evolution of CO_2 and thioamide **2** is obtained as the product. In the case of anisole and phenetole, however, even the use of 4 mol of $AlCl_3$ or a reaction temperature of 100 °C fails to yield any of the thioamide. In general, a molar ratio of catalyst to isothiocyanate larger than 2:1 does not improve significantly the yield of either product. When monosubstituted benzenes are used as reagents, the major product arises from electrophilic attack at the para position relative to the original substituent, as has been observed in other similar reactions.[1,2] No attempt has been made in this study to identify or isolate any product corresponding to reaction at the ortho position of the aromatic ring.

Tables I and II display some physical and spectral constants of the compounds prepared, as well as the particular methods and yields of their preparation.

The nature of the product appears to be controlled mainly by two factors, the quantity of catalyst and the reaction temperature. For thioamide to be the major product, a molar ratio of $AlCl_3$ to isothiocyanate equal to at least 2:1 must be used. On the other hand, a low reaction temperature clearly favors the *N*-ethoxycarbonylthioamide. To a smaller extent, the outcome of the reaction also depends on its duration (a longer period of time favoring the thioamide) and the nature of the aromatic compound.

With regard to the formation of thioamide, it may be concluded that this results from further reaction of the originally formed *N*-ethoxycarbonyl derivative. This conclusion is supported by the formation of thiobenzamide as the only isolable product when the reaction of benzene is run under conditions which normally lead to compound **1a** (equimolar amounts of reagents, CH_2Cl_2 as solvent, 0–3 °C) but, before hydrolysis, a second equivalent of benzene is added and the reaction allowed to proceed at reflux.

The *N*-ethoxycarbonylthioamide formed in these reactions can be expected to be coordinated with $AlCl_3$ at the sulfur atom. In the presence of enough catalyst, further coordination at the carbonyl oxygen yields a strongly electrophilic ester group capable of reacting with the ring of the aromatic reagent in a Friedel–Crafts manner. Although such a reaction is also possible at the carbonyl carbon atom, it actually appears to occur at the α carbon of the ethyl group and to result in alkylation of the aromatic ring. The carbamate complex formed at the same time is later hydrolyzed to the corresponding carbamic acid which decarboxylates giving off CO_2.

The proposed interpretation of thioamide formation finds support in the known alkylation of aromatic compounds by treatment with esters and $AlCl_3$.[4,5] It is also consistent with the presence of ethylbenzene in the organic distillate obtained during isolation of the product, when benzene has reacted to form thiobenzamide. The fact that ethylbenzene is found by gas chromatography in about one-half of the theoretical amount may be attributed to its further alkylation, as well as reaction with the isothiocyanate. Indeed, the gas chromatogram of the organic distillate contains several minor peaks with retention times longer than that of ethylbenzene. Also, the NMR spectrum of crude thiobenzamide indicates the presence of a small quantity of *p*-ethylthiobenzamide. Significant reaction at the carbonyl carbon may be excluded, in view of the absence of a peak corresponding to ethyl benzoate from the above gas chromatogram. Furthermore, such a reaction would be inconsistent with formation of CO_2 during hydrolysis of the product. When chlorobenzene reacts to form 4-chlorothiobenzamide and the gases evolved upon hydrolysis are led through an aqueous $Ba(OH)_2$ solution, $BaCO_3$ is collected in about 90% of the theoretical amount. Finally, the observed diminishing tendency to yield the thioamide,

Table II[a]

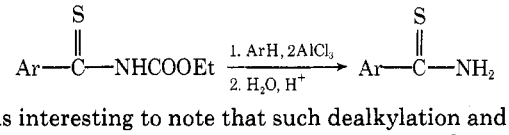
S
‖
Ar—C—NH_2

2	Ar	Method	% yield[b]	Mp, °C	Ir, cm^{-1} NH	Ir, cm^{-1} NH_2[c]	NMR, ppm NH_2	NMR, ppm Aromatic ring	NMR, ppm R[d]
a	C_6H_5	A, C, D	80–87	114–116[e]	3370, 3280, 3160	890	9.2 (s, 1), 9.6 (s, 1)	7.6–7.8 (m, 2), 7.1–7.3 (m, 3)	
b	4-MeC_6H_4	A, B	56–58	168–169[f]	3380, 3260, 3160	890	9.2 (s, 1), 9.5 (s, 1)	7.7 (m, 2), 7.0 (m, 2)	2.3 (s, 3)
c	4-EtC_6H_4	A	56	139–140	3360, 3270, 3150	890	9.2 (s, 1), 9.5 (s, 1)	7.7 (m, 2), 7.0 (m, 2)	2.6 (q, 2), 1.2 (t, 3)
d	4-*i*-PrC_6H_4[g]	A	62	147–148.5	3300–3140	900	9.2 (s, 1), 9.5 (s, 1)	7.7 (m, 2), 7.0 (m, 2)	2.8 (m, 1), 1.2 (d, 6)
e	4-*t*-BuC_6H_4	B	56	145.5–147.5	3380, 3270, 3130	900	9.2 (s, 1), 9.5 (s, 1)	7.7 (m, 2), 7.2 (m, 2)	1.3 (s, 9)
f	2,5-$DiMeC_6H_3$	A	86	94–96	3290, 3260	850	9.2 (s, 1), 9.7 (s, 1)	6.9 (s, 3)	2.2 (s, 6)
g	2,4,6-$TriMeC_6H_2$	A	91	208–210 dec	3370, 3250, 3120	890	9.2 (s, 1), 9.7 (s, 1)	6.7 (s, 2)	2.2 (s, 9)
h	4-$MeOC_6H_4$	F	79	148–149.5[h]	3360, 3280, 3160	890	9.1 (s, 1), 9.4 (s, 1)	7.8 (m, 2) 6.8 (m, 2)	3.8 (s, 3)
i	4-$EtOC_6H_4$	F	84	157.5–159[i]	3350, 3280	890	9.1 (s, 1), 9.4 (s, 1)	7.8 (m, 2) 6.8 (m, 2)	4.0 (q, 2), 1.3 (t, 3)
j	4-ClC_6H_4	B, C, D, E	61–64	127.5–129.5[j]	3250, 3130	890	9.5 (s, 2)	7.8 (m, 2), 7.3 (m, 2)	
k	4-BrC_6H_4	B, E	56–60	141.5–143[k]	3380, 3290, 3170	890	9.3 (s, 1), 9.4 (s, 1)	7.7 (m, 2), 7.4 (m, 2)	

[a] Satisfactory analytical data (±0.3% for C, H, N) were reported for all new compounds listed in this table. [b] Crude or partially purified product with melting point lower than that of the analytical sample by 2–10 °C. [c] NH_2 bending mode (wagging): K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, **20**, 597 (1966). This characteristic band of primary thioamides (absent from the spectra of the corresponding carboxamides) had earlier been attributed to C=S stretching: L. J. Bellamy and P. E. Rogasch, *J. Chem. Soc.*, 2218 (1960). [d] Alkyl or alkoxy substituent(s) attached to the aromatic ring. [e] Lit. mp 116–117°: M. M. Endicott, E. Wick, M. L. Mercury, and M. L. Sherril, *J. Am. Chem. Soc.*, **68**, 1299 (1946). [f] Lit. mp 168°: Paterno and Spica, *Ber.*, **8**, 441 (1875). [g] E. Czumpelik, *Ber.*, **2**, 185 (1869). [h] Lit. mp 154°: S. Kakimoto, J. Seydel, and E. Wempe, *Arzneim.-Forsch.*, **12**, 127 (1962); *Chem. Abstr.*, **57**, 9812*i* (1952). [i] Lit. mp 162°: reference in *h*. [j] Lit. mp 124°: K. Kindler, *Justus Liebigs Ann. Chem.*, **450**, 1 (1926). [k] Lit. mp 141.5°: reference in *j*.

benzene, alkylbenzenes > halobenzenes ≫ alkoxybenzenes, parallels the increasing ability of the substituent of the aromatic reagent to coordinate with $AlCl_3$ and, therefore, the expected decreasing availability of $AlCl_3$ for coordination with the carbonyl oxygen.

Consistent with the previous arguments concerning the dealkylation and decarboxylation reactions is the following observation. If a solution of *N*-ethoxycarbonylthiobenzamide (**1a**) in benzene is mixed with 2 molar equiv of $AlCl_3$ and heated on a steam bath for 3–4 min, or let stand at room temperature for 4 h, hydrolysis of the mixture with ice and hydrochloric acid causes CO_2 evolution and precipitation of thiobenzamide. In both cases, the organic layer is found by gas chromatography to contain ethylbenzene. This seems to be a general reaction of *N*-ethoxycarbonylthioamides and provides a simple and efficient method for their conversion into the corresponding thioamides.



It is interesting to note that such dealkylation and decarboxylation of the anisole derivative **1h** proceed to a minor extent only upon brief heating with benzene and 2 mol of $AlCl_3$, but to completion when 3 mol of $AlCl_3$ are used. No reaction occurs when anisole is used instead of benzene. The results agree with the expected strong coordination of $AlCl_3$ with the methoxy group and are consistent with the earlier mentioned exclusive formation of the *N*-ethoxycarbonyl derivative **1h** or **1i** when anisole or phenetole react with EtOOC–NCS even under conditions which in all other cases lead to thioamides.

In conclusion, the reaction which has been described allows preparation of certain thioamides in one step from the corresponding aromatic compounds. It is subject to the usual limitations of the Friedel–Crafts reactions but, because of its simplicity and satisfactory yields, it compares favorably with other methods of preparation of thioamides[6–8] which are useful starting materials for the synthesis of various heterocyclic compounds.[6–8]

Under somewhat different conditions, the same reaction affords *N*-ethoxycarbonyl derivatives of aromatic thioamides in fair to good yields. When both types of compounds are present in the product, their separation from each other is easy, because thioamides are only sparingly soluble in dilute aqueous NaOH, whereas their *N*-ethoxycarbonyl derivatives dissolve easily in it and may subsequently be recovered by acidification of the alkaline solution. In addition to the earlier discussed dealkylation and decarboxylation by the action of $AlCl_3$ and an aromatic compound, *N*-ethoxycarbonylthioamides undergo as expected[9] the same overall reaction when treated with aqueous alkali. For a good yield of thioamide, however, this reaction must be run at room temperature over a relatively long period of time (48–72 h) because heating results in formation of the corresponding nitrile as by-product.

Experimental Section[10]

Preparation of *N*-Ethoxycarbonylthioamides (1). A. To a stirred cold (ice bath) solution of 0.050 mol of the aromatic compound and 6.5 g (0.050 mol) of ethoxycarbonyl isothiocyanate in 30 ml of CH_2Cl_2 was added 13.3 g (0.10 mol) of anhydrous $AlCl_3$, in small portions[11] (15–20 min) at 0–3°C. The reaction mixture was stirred at this temperature for 4 h and then it was hydrolyzed by careful addition of ice and dilute hydrochloric acid. Enough

CH_2Cl_2 was added to dissolve any solid organic material and the resulting solution was extracted with four 50-ml portions of 10% aqueous NaOH. This extract was washed with ethyl ether and acidified with concentrated hydrochloric acid (ice bath) to yield an oil which solidified upon cooling. The solid material was washed successively with dilute hydrochloric acid and water, dried, and washed again with petroleum ether (bp 30–60 °C), or cold ethyl ether, or cold aqueous ethanol. Purification of the crude product was accomplished by recrystallization from petroleum ether (bp 30–60 or 60–75 °C), benzene–petroleum ether (bp 60–75 °C), cyclohexane, or aqueous ethanol.

B. As in A, except that 10.0 g (0.075 mol) of $AlCl_3$ was used and the reaction mixture was stirred at 0–3 °C for 2 h after addition of the catalyst and before hydrolysis.

C. Anhydrous $AlCl_3$ (13.3 g, 0.10 mol) was added in one portion to 75 ml of the cold (ice bath) aromatic compound and a solution of 6.5 g (0.050 mol) of EtOOC–NCS in 25 ml of the aromatic compound was allowed to flow slowly (15–20 min) into the stirred slurry. The resulting mixture was stirred at 0–3 °C for 1 h, then the cooling bath was removed and stirring continued for a further 4 h. The subsequent treatment was as in A, except that ethyl ether was used to dissolve the organic materials following hydrolysis and prior to extraction with aqueous alkali.

D. As in C, except that the cooling bath was removed upon completion of addition of the isothiocyanate and the reaction mixture stirred for 6 h at room temperature.

E. As in C except that the reaction mixture was stirred at 0–3 °C for 6 h following addition of the isothiocyanate and prior to hydrolysis.

Preparation of Thioamides (2). A. Anhydrous $AlCl_3$ (13.3 g, 0.10 mol) was added in one portion to 75 ml of the cold (ice bath) aromatic compound and the resulting mixture was stirred for 1–2 min. The cooling bath was then removed and a solution of 6.5 g (0.050 mol) of ethoxycarbonyl isothiocyanate in 25 ml of the aromatic compound was allowed to flow slowly (15–20 min) into the stirred slurry. Following completion of this addition, the reaction mixture was stirred for 4 h and then it was cooled (ice bath) again and hydrolyzed by careful addition of a mixture of ice and dilute hydrochloric acid. Enough ethyl ether was added to dissolve any solid organic material and the resulting solution was washed successively with 10% aqueous NaOH and water. After it had been dried ($MgSO_4$), this solution was concentrated under reduced pressure and the precipitated solid was collected by filtration and washed with petroleum ether (bp 30–60 °C), or cold CCl_4, or cold aqueous ethanol. The crude product was then purified by recrystallization from EtOH–H_2O or benzene–petroleum ether (bp 60–75 °C).

B. As in A except that following addition of the isothiocyanate the reaction mixture was stirred at room temperature for 1 h and then on the steam bath for a further 2–3 h.

C. As in A except that $AlCl_3$ was added without cooling to a solution of 6.5 g of EtOOC–NCS in 100 ml of the aromatic compound and the reaction mixture was stirred first without external heating for 1 h and then on the steam bath for an additional 1 h.

D. As in C except that 20.0 g of $AlCl_3$ was used.

E. As in C except that the reaction mixture was stirred only at room temperature, for 24 h.

F. A solution of 1.0 g of *N*-ethoxycarbonylthioamide in 10 ml of 10% aqueous NaOH was let stand at room temperature for 48–72 h. The precipitated solid was collected, washed with water, mixed with dilute hydrochloric acid, collected again by filtration, and finally washed with water.

Dealkylation and Decarboxylation of *N*-Ethoxycarbonylthioamides. A mixture of 5 mmol of **1**, 10 mmol of $AlCl_3$, and 5 ml of benzene was stirred on the steam bath for 3 min, then it was chilled and decomposed by addition of ice and dilute hydrochloric acid. The hydrolysis product was mixed with petroleum ether (bp 30–60 °C) and the precipitated **2** was collected by filtration and washed with water. Yields: **2a**, 75%; **2d**, 77%; **2h** (use of 15 mmol of $AlCl_3$), 71%; thiophene-2-thioamide (use of 15 mmol of $AlCl_3$), 89%.

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Registry No.—1a, 5499-31-0; **1b,** 57774-66-0; **1c,** 57774-67-1; **1d,** 57774-68-2; **1e,** 57774-69-3; **1f,** 57774-70-6; **1g,** 57774-71-7; **1h,** 57774-72-8; **1i,** 57774-73-9; **1j,** 57774-74-0; **1k,** 57774-75-1; **2a,** 2227-79-4; **2b,** 2362-62-1; **2c,** 57774-76-2; **2d,** 53515-20-1; **2e,** 57774-77-3; **2f,** 57774-78-4; **2g,** 57182-71-5; **2h,** 2362-64-3; **2i,** 57774-79-5; **2j,** 2521-24-6; **2k,** 26197-93-3; ArH (Ar = C_6H_5), 71-43-2; ArH (Ar = 4-MeC_6H_4), 108-88-3; ArH (Ar = 4-EtC_6H_4), 100-41-4; ArH (Ar = 4-*i*-PrC_6H_4), 98-82-8; ArH (Ar = 4-*t*-BuC_6H_4), 98-06-6; ArH (Ar = 2,5-diMeC_6H_3), 106-42-3; ArH (Ar = 2,4,6-triMeC_6H_2) 108-67-8; ArH (Ar = 4-$MeOC_6H_4$), 100-66-3; ArH (Ar = 4-$EtOC_6H_4$), 103-73-1; ArH (Ar = 4-ClC_6H_4), 108-90-7; ArH (Ar = 4-BiC_6H_4), 108-86-1; ethoxycarbonyl isothiocyanate, 16182-04-0.

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