the ^{13}C NMR spectrum had extra aliphatic peaks still present. The HRMS showed a molecular ion peak, which was also the base peak, with the correct exact mass: ^1H NMR ($CDCl_3$) δ 7.0–7.3 (m, 4 H), 6.7–7.0 (m, 4 H), 4.5–5.0 (m, 2 H), 2.0–2.5 (m, 4 H), 0.7–1.7 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 146.3, 145.4, 142.0, 139.6, 124.2, 122.7, 122.3, 57.5, 55.7, 55.4, 44.6, 33.0, 31.6, 30.3, 29.3, 25.3, 22.4, 14.1, 9.2; MS (EI, 70 eV, 170 °C) *m/e* (%) 350 (M^+, 100), 216 ($C_{17}H_{12}$, 100), 215 ($C_{17}H_{11}$, 31), 192 ($C_{15}H_{12}$, 30), 179 ($C_{14}H_{11}$, 36), 178 ($C_{14}H_{10}$, 99); HRMS calcd for $C_{27}H_{28}$ 350.2032, found 350.2033.

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A New Synthetic Route to the Previously Unattainable 2-Arylpyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-ones

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A variety of 2-arylpyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-ones has been efficiently synthesized by treatment of the anion of 2-chloro-3-(*N*-methylacetamido)- and -3-acetamidopyridine with the appropriate *O*-ethyl thiocarboxylates.

In recent years members of the benzothiazepinone class of compounds have generated considerable interest owing to their remarkable diversity of biological activity. In particular, the 2-aryl-1,5-benzothiazepin-4(5*H*)-one skeleton constitutes the framework of several biologically active compounds, e.g., antidepressants like Thiazesim,[1] coronary vasodilators like Diltiazem,[2,3] and antiulcer and antisecretory agents such as BTM-1086.[4] Paradoxically, despite the considerable development of procedures for efficiently constructing nitrogen-containing rings, the pyridothiazepinone skeleton still remains difficultly accessible. To our knowledge the only reported method for the elaboration of this polyheterocyclic system consists of treating 2-mercapto-3-aminopyridine with 3-bromopropanoic acid.[5] However, the method is not general in scope and is rather restrictive, especially with regard to the eventual introduction of various substituents in the seven-membered heterocyclic moiety.

In this paper we report a novel, general and effective synthetic approach to the previously unattainable N-substituted or unsubstituted 2-arylpyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-ones **6a–g** and **7a–c**. Our strategy consists of reacting aromatic thiocarboxylates **4a–g** with the anion of 2-chloro-3-(*N*-methylacetamido)- or -3-acetamidopyridine, (**1** and **2**), respectively (Scheme I).

The *O*-ethyl thiocarboxylates **4a–g** are efficiently prepared by treatment of aromatic and heteroaromatic carboximidic acid esters, readily accessible from the appropriate nitriles via the Pinner reaction, with hydrogen sulfide at low temperature.[6] The anion of 2-chloro-3-(*N*-methylacetamido)pyridine (**1**) is generated by treatment with 1.1 molar equiv of lithium diisopropylamide (LDA) in tetrahydrofuran (THF). This metalation reaction must be carried out at −78 °C to prevent thermal decomposition of the intermediate carbanion.[7] The addition of the ap-

Scheme I

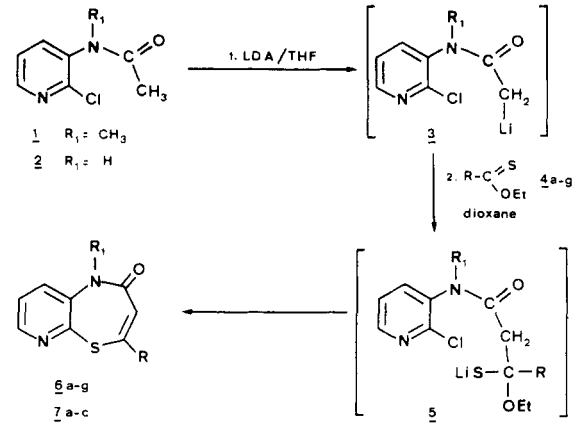
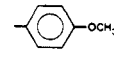
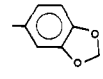
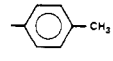
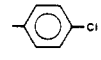


Table I. 2-Substituted Pyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-ones from Condensation of Lithiated Acetamidopyridines with Thioesters

amide		thioester 4, R =	product	yield (%)
1 (R_1 = CH_3)	a		6a	59
1	b		6b	57
1	c		6c	66
1	d		6d	61
1	e		6e	60
1	f		6f	59
1	g		6g	61
2 (R_1 = H)	a	4a	7a	56
2	b	4b	7b	55
2	c	4c	7c	61

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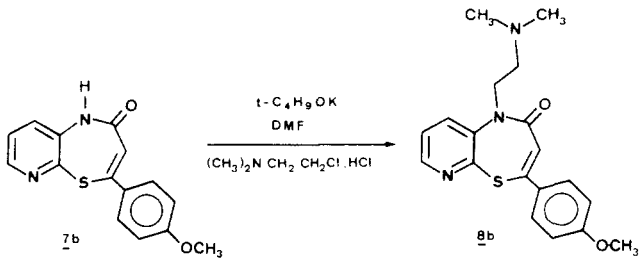
Scheme II



propriate thioesters is also effected at −78 °C but the insertion of the sulfur atom giving rise to the annelation products **6a–g** occurs after warming to ambient temperature, replacement of THF by dioxane, and refluxing in dioxane for 4 h. Results of a representative series of reactions are presented in Table I, where it may be seen that this simple procedure affords generally good yields of pyrido[2,3-*b*]thiazepinones with various aryl substituents at position 2. The structure of **6** was determined by ^{1}H NMR spectroscopy, which principally indicates the presence of one olefinic proton α to the carbonyl group at δ 6.55 (value given for **6c**). It was confirmed by 100-MHz ^{13}C NMR spectroscopy and by comparison of DEPT spectra with different pulse angles θ, which unambiguously establishes the presence for **6c** of one methyl (δ 36.9), one methylene (δ 101.7), seven methine (δ 106.9, 108.2, 122.4, 122.7, 124.7, 133, 145.7), and seven quaternary carbon atoms (δ 130.9, 140.8, 146.7, 147.9, 149.1, 152.8, 166.1).

The unsubstituted pyridothiazepinones **7a–c** (Scheme I) are accessible in a similar way from 2-chloro-3-acetamidopyridine (**2**). Due to the presence of two deprotonation sites in **2**, the metalation reaction requires 2 molar equiv of LDA. The observed preferential condensation of the electrophilic thiocarbonyl compounds **4a–c** at the α-carbon of the dilithioamide **3** (R_1 = Li) rather than at the amido nitrogen is not surprising since the anion formed by the secondary ionization might be expected to be more nucleophilic. The yields for the obtention of the fused heterocyclic models **7a–c** are not affected by this double metalation operation (Table I).

From a mechanistic point of view it is likely that the reactions described in Scheme I proceed via the intermediacy of the transient sulfur anion **5**. The annelation reaction that gives rise to **6a–g** and **7a–c** is actually the combined result of the remarkable nucleophilicity of the intermediate sulfur anion and of the great sensitivity of the chlorine atom in 2-chloropyridines with respect to nucleophilic attacks. The absence of 5-*exo-trig* cyclization products arising from nucleophilic substitution by the carboxamide α-anion is logical since it has been elegantly demonstrated that this type of substitution must be imperatively photostimulated.[7]

The presence of the (dimethylamino)ethyl group in the biologically active models such as Diltiazem and Thiazesim led us to consider the introduction of this pattern in the parent model **7**. After experimenting with a variety of conditions and methods, it was found that the best result for the N-functionalization of the unsubstituted model **7b** was obtained following a method recently described for the alkylation of benzothiazinones.[8] The procedure makes use of potassium *tert*-butoxide as the base in dimethylformamide at room temperature (Scheme II). 5-[2-(Dimethylamino)ethyl]-2-(*p*-methoxyphenyl)pyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-one (**8b**) is then obtained with the moderate yield of 72%.

In conclusion, the reaction of aromatic thioesters with the carbanions of 2-chloro-3-(*N*-methylacetamido) and -3-acetamidopyridine offers a convenient and effective synthetic route to the barely accessible 2-arylpyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-ones. The method illustrates the great versatility of aromatic thiocarboxylates in the elaboration of five-,[9,10] six-,[11] and seven-membered rings.

Experimental Section

General Techniques. Melting points are uncorrected. ^{1}H NMR (80 MHz) spectra were run on a Bruker WP 80 spectrometer. IR spectra were recorded on a Perkin-Elmer 881 instrument. Mass spectra were registered on a Riber 10-10 apparatus. For column chromatography, Merck 70–230-mesh aluminum oxide 90 basic was employed. Elemental analyses were performed at the CNRS microanalysis center.

Starting Materials. The 2-chloro-3-(*N*-methylacetamido) and 2-chloro-3-acetamidopyridines (**1** and **2**), respectively, were synthesized according to standard procedures.[7]

The aromatic and heteroaromatic *O*-ethyl thiocarboxylates **4a–g** were prepared by treatment of the corresponding carboximidates with hydrogen sulfide. Initially, aromatic and heteroaromatic nitriles (0.15 mol) were treated with ethanol (2 equiv) and hydrogen chloride (0.19 mol) in chloroform (30 mL) at 0 °C. After 5 days in the refrigerator the salts of the carboximidic acid esters were washed with anhydrous diethyl ether and treated with ammonia, which gave the desired carboximidates in nearly quantitative yields.[6]

The thiocarboxylates **4a–g** were obtained in the following manner: dried cation exchange resin (Dowex 50W-X8, H^+, 16 g, 80 mmol) was added to a solution of the appropriate carboximidic acid ester (50 mmol) in dry methanol (200 mL). The reaction mixture was stirred rapidly and cooled to −30 °C in an acetone–dry ice slush bath. Then hydrogen sulfide gas was passed through the mixture for 30 min and stirring was maintained for an additional hour at −20 °C. The reaction mixture was filtered, and the filtrate was evaporated in vacuo to furnish quantitative yields of the aromatic thiocarboxylates **4a–g**, which were distilled immediately before use.

Preparation of 2-Arylpyrido[2,3-*b*][1,5]thiazepin-4-(5*H*)-ones 6a–g and 7a–c; General Procedure. A solution of LDA was prepared at −78 °C by addition, with stirring and under argon, of a solution of diisopropylamine (1.7 mL, 10 mmol) in 10 mL of THF to 6.3 mL of 1.6 M *n*-butyllithium in hexane diluted with 10 mL of anhydrous THF. A solution of the acetamidopyridines **1** (9 mmol) or **2** (4.5 mmol) in 5 mL of THF was added dropwise at such a rate as to maintain the internal temperature below −70 °C. The reaction mixture (straw yellow for **1** and deep orange for **2**) was stirred under argon for an additional 30 min. A solution of the thioesters **4a–g** (10 or 5 mmol) in 5 mL of THF was then added. The cooling bath was removed, and the mixture was warmed rapidly to ambient temperature and then gently refluxed. A brisk stream of dried argon was passed through the system to evaporate the solvents (hexane, THF), which were carefully replaced by 20 mL of freshly distilled dioxane. The reaction mixture was refluxed for 4 h and, after cooling, was poured into crushed ice. In all cases compounds **6a–g** and **7a–c** separate out as solids. The yields reported in Table I have been determined after recrystallization.

***N*-Methyl-2-phenylpyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-one (6a)**: mp 158–159 °C (hexane–toluene); MS *m/z* (relative intensity) 268 (M^+, 100), 240 (M^+ − CO, 69), 211 (M^+ − CH_3NCO, 15); IR (KBr) 1660 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.4 (s, 3 H, NCH_3), 6.5 (s, 1 H, HC=C), 7.2–7.9 (m, 7 H, aromatic CH), 8.3 (dd, 1 H, J = 4.4 Hz, 1.8 Hz, pyridine CH). Anal. Calcd for $C_{15}H_{12}N_2OS$: C, 67.16; H, 4.48; N, 10.45; O, 5.97; S, 11.94. Found: C, 67.16; H, 4.47; N, 10.51; O, 6.21; S, 12.01.

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***N*-Methyl-2-(4-methoxyphenyl)pyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-one (6b)**: mp 160–161 °C (hexane–toluene); MS *m/z* (relative intensity) 298 (M^+, 50), 270 (M^+ – CO, 80), 241 (M^+ – CH_3NCO, 90); IR (KBr) 1660 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 3.4 (s, 3 H, NCH_3), 3.8 (s, 3 H, OCH_3), 6.4 (s, 1 H, HC=C), 6.8 (d, 2 H, *J* = 9 Hz, aromatic CH), 7.2–7.8 (m, 4 H, aromatic CH), 8.3 (dd, *J* = 4.4 Hz, 1.7 Hz, 1 H, pyridine CH). Anal. Calcd for $C_{16}H_{14}N_2O_2S$: C, 64.43; H, 4.70; N, 9.40; O, 10.74; S, 10.74. Found: C, 64.35; H, 4.71; N, 9.25; O, 11.06; S, 11.02.

***N*-Methyl-2-(3,4-(methylenedioxy)phenyl)pyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-one (6c)**: mp 212–213 °C (ethanol–dimethylformamide); MS *m/z* (relative intensity) 312 (M^+, 54), 284 (M^+ – CO, 100); ^1H NMR (80 MHz, d_6-DMSO) δ 3.4 (s, 3 H, NCH_3), 6.1 (s, 2 H, OCH_2O), 6.55 (s, 1 H, HC=C), 7.0 (d, *J* = 8 Hz, 1 H, aromatic CH), 7.3–7.5 (m, 3 H, aromatic CH), 8.0 (d, *J* = 10 Hz, 1 H, pyridine CH), 8.35 (dd, *J* = 4.6, 1.6 Hz, 1 H, pyridine CH). Anal. Calcd for $C_{16}H_{12}N_2O_3S$: C, 61.53; H, 3.87; N, 8.97; O, 15.37; S, 10.26. Found: C, 61.58; H, 4.00; N, 8.67; O, 15.54; S, 10.00.

***N*-Methyl-2-(4-methylphenyl)pyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-one (6d)**: mp 173–175 °C (hexane–toluene); MS *m/z* (relative intensity) 282 (M^+, 80), 254 (M^+ – CO, 100), 225 (M^+ – CH_3NCO, 40); IR (KBr) 1660 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 2.3 (s, 3 H, CH_3), 3.4 (s, 3 H, NCH_3), 6.4 (s, 1 H, HC=C), 7.2–7.8 (m, 6 H, aromatic CH), 8.3 (dd, *J* = 4.4, 1.7 Hz, 1 H, pyridine CH). Anal. Calcd for $C_{16}H_{14}N_2OS$: C, 68.08; H, 4.96; N, 9.93; O, 5.67; S, 11.35. Found: C, 67.63; H, 5.02; N, 9.70; O, 5.88; S, 11.38.

***N*-Methyl-2-(4-chlorophenyl)pyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-one (6e)**: mp 192–194 °C (hexane–toluene); MS *m/z* (relative intensity) 304 (M^+, 22), 302 (M^+, 60), 276 (M^+ – CO, 100); IR (KBr) 1658 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 3.4 (s, 3 H, CH_3), 6.4 (s, 1 H, HC=C), 7.2–7.8 (m, 6 H, aromatic CH), 8.3 (dd, *J* = 4.4, 1.7 Hz, 1 H, pyridine CH). Anal. Calcd for $C_{15}H_{11}N_2OSCl$: C, 59.44; H, 3.64; N, 9.26; O, 5.29; S, 10.58; Cl, 11.74. Found: C, 59.23; H, 3.69; N, 9.04; O, 5.73; S, 10.58; Cl, 11.82.

***N*-Methyl-2-(2-furyl)pyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-one (6f)**: mp 163–164 °C (hexane–toluene); MS *m/z* (relative intensity) 258 (M^+, 100), 230 (M^+ – CO, 84), 201 (M^+ – CH_3NCO, 60); IR (KBr) 1660 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 3.4 (s, 3 H, CH_3), 5.3 (dd, *J* = 3.5, 1.8 Hz, 1 H, furan CH), 6.6 (s, 1 H, HC=C), 7.0 (d, *J* = 3.5 Hz, 1 H, furan CH), 7.1–7.7 (m, 3 H, aromatic CH), 8.3 (dd, *J* = 4.4, 1.7 Hz, pyridine CH). Anal. Calcd for $C_{13}H_{10}N_2O_2S$: C, 60.47; H, 3.88; N, 10.85; O, 12.40; S, 12.40. Found: C, 60.23; H, 3.94; N, 10.60; O, 12.73; S, 12.59.

***N*-Methyl-2-(2-thienyl)pyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-one (6g)**: mp 177–179 °C (hexane–toluene); MS *m/z* (relative intensity) 274 (M^+, 85), 246 (M^+ – CO, 55), 217 (M^+ – CH_3NCO, 35); IR (KBr) 1658 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 3.4 (s, 3 H, NCH_3), 6.5 (s, 1 H, HC=C), 7.01 (dd, *J* = 5.2, 3.8 Hz, 1 H, thiophene CH), 7.2–7.7 (m, 4 H, aromatic CH), 8.3 (dd, *J* = 4.4, 1.7 Hz, 1 H, pyridine CH). Anal. Calcd for $C_{13}H_{10}N_2OS_2$: C, 56.93; H, 3.65; N, 10.22; O, 5.84; S, 23.36. Found: C, 56.68; H, 3.61; N, 9.91; O, 6.17; S, 23.35.

2-Phenylpyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-one (7a): mp 226–228 °C (dimethylformamide); MS *m/z* (relative intensity) 254 (M^+, 100), 226 (M^+ – CO, 70); IR (KBr) 3130, 1665 cm^{-1}; ^1H NMR (80 MHz, d_6-DMSO) δ 6.6 (s, 1 H, HC=C), 7.0–8.1 (m, 7 H, aromatic CH), 8.3 (dd, *J* = 4.2, 2.0 Hz, 1 H, pyridine CH), 10.5 (s, 1 H, NH). Anal. Calcd for $C_{14}H_{10}N_2OS$: C, 66.14; H, 3.94; N, 11.02; O, 6.30; S, 12.60. Found: C, 66.27; H, 3.82; N, 11.35; O, 6.52; S, 13.01.

2-(4-Methoxyphenyl)pyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-one (7b): mp 238–240 °C (dimethylformamide); MS *m/z* (relative intensity) 284 (M^+, 100), 256 (M^+ – CO, 60); IR (KBr) 3130, 1665 cm^{-1}; ^1H NMR (80 MHz, d_6-DMSO) δ 3.8 (s, 3 H, OCH_3), 6.6 (s, 1 H, HC=C), 7.1 (d, *J* = 9 Hz, 1 H, aromatic CH), 7.4–8.1 (m, 3 H, aromatic CH), 8.3 (dd, *J* = 4.2, 2.0 Hz, 1 H, pyridine CH), 10.5 (s, 1 H, NH). Anal. Calcd for $C_{15}H_{12}N_2O_2S$: C, 63.38; H, 4.22; N, 9.86; O, 11.27; S, 11.27. Found: C, 63.01; H, 4.57; N, 9.93; O, 11.62; S, 11.35.

2-(3,4-(Methylenedioxy)phenyl)pyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-one (7c): mp 315–316 °C (dimethylformamide); MS *m/z* (relative intensity) 298 (M^+, 100), 270 (M^+ – CO, 34); IR (KBr) 3130, 1665 cm^{-1}; ^1H NMR (80 MHz, d_6-DMSO) δ 6.1 (s, 2 H, OCH_2O), 6.55 (s, 1 H, HC=C), 7.0 (d, *J* = 8 Hz, 1 H, aromatic CH), 7.3–7.6 (m, 4 H, aromatic CH), 8.3 (dd, *J* = 4.5, 1.6 Hz, 1 H, pyridine CH), 10.45 (s, 1 H, NH). Anal. Calcd for $C_{15}H_{10}N_2O_3S$: C, 60.39; H, 3.38; N, 9.39; O, 16.09; S, 10.75. Found: C, 60.08; H, 3.42; N, 9.22; O, 16.35; S, 10.69.

N-Alkylation of 2-(*p*-Methoxyphenyl)pyrido[2,3-*b*][1,5]thiazepin-4(5*H*)-one (7b). Compound **7b** (1 g, 3.5 mmol) and 2-(dimethylamino)ethyl chloride hydrochloride (0.5 g, 3.5 mmol) were combined and dissolved in dry dimethylformamide (35 mL). Freshly sublimed potassium *tert*-butoxide (1 g, 8.9 mmol) was then added and the reaction mixture was stirred under argon for 3 days at room temperature. The dimethylformamide was removed in vacuo. Water (20 mL) was then added and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The organic extracts were washed with water (100 mL) and dried with magnesium sulfate. After removal of the solvent the crude product was purified by column chromatography on alumina using a mixture of hexane–ethyl acetate (2:3) as eluent. Recrystallization of the product from hexane–toluene furnished 760 mg (yield 72%) of 5-(2-(dimethylamino)ethyl)-2-(4-methoxyphenyl)pyrido[2,3-*b*]-[1,5]thiazepin-4(5*H*)-one (**8b**): mp 99–101 °C; MS *m/z* (relative intensity) 355 (M^+, 80), 58 ($CH_2N(CH_3)_2$, 100); IR (KBr) 1665 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 2.2 (s, 6 H, NCH_3), 2.5 (m, 2 H, CH_2), 3.8 (s, 3 H, OCH_3) 4.0 (m, 2 H, CH_2), 6.4 (s, 1 H, HC=C), 6.8 (d, *J* = 9 Hz, 2 H, aromatic CH), 7.3 (m, 1 H, pyridine CH), 7.6–7.9 (m, 3 H, aromatic CH), 8.3 (dd, *J* = 4.4, 1.7 Hz, 1 H, pyridine CH). Anal. Calcd for $C_{19}H_{21}N_3O_2S$: C, 64.23; H, 5.92; N, 11.83; O, 9.01; S, 9.01. Found: C, 64.55; H, 5.93; N, 12.01; O, 9.27; S, 8.87.

Registry No. 1, 74585-37-8; **2**, 21352-19-2; **4a**, 936-61-8; **4b**, 10602-66-1; **4c**, 117666-92-9; **4d**, 26028-04-6; **4e**, 13915-60-1; **4f**, 13749-75-2; **4g**, 13749-76-3; **6a**, 127129-99-1; **6b**, 127130-00-1; **6c**, 127130-01-2; **6d**, 127130-02-3; **6e**, 127130-03-4; **6f**, 127130-04-5; **6g**, 127130-05-6; **7a**, 127130-06-7; **7b**, 127130-07-8; **7c**, 127130-08-9; **8b**, 127130-09-0; C_6H_5CN, 100-47-0; $4\text{-}CH_3OC_6H_4CN$, 874-90-8; $4\text{-}CH_3C_6H_4CN$, 104-85-8; $4\text{-}ClC_6H_4CN$, 623-03-0; $C_6H_5C(OEt)$=NH, 825-60-5; $4\text{-}CH_3OC_6H_4C(OEt)$=NH, 829-48-1; $4\text{-}CH_3C_6H_4C(OEt)$=NH, 827-71-4; $4\text{-}ClC_6H_4C(OEt)$=NH, 827-72-5; $(CH_3)_2N(CH_2)_2Cl$, 107-99-3; 1,3-benzodioxole-5-carbonitrile, 4421-09-4; 2-furancarbonitrile, 617-90-3; 2-thiophenecarbonitrile, 1003-31-2; ethyl 1,3-benzodioxole-5-carboximidate, 55308-42-4; ethyl 2-furancarboximidate, 39606-85-4; ethyl 2-thiophenecarboximidate, 54610-47-8.