

PREPARATION OF *N*'-ALKYL- AND *N*',*N*'-DIALKYLISOQUINOLINE-1,3-DIAMINES AND 1-ALKYL- AND 1-PHENYLISOQUINOLIN-3-AMINES FROM THE REACTION OF α -CYANO-*o*-TOLUNITRILE WITH LITHIUM AMIDES, ALKYL LITHIUMS, AND PHENYL LITHIUM

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Abstract – A facile, one-step synthesis of the titled compounds from the reaction of α -cyano-*o*-tolunitrile with LiNHR, LiNRR', RLi, or PhLi is described. A mechanism is presented in which α -cyano-*o*-tolunitrile is first converted quantitatively to its ketenimine carbanion by the lithium base. The remaining aromatic cyano group on the ketenimine carbanion then undergoes nucleophilic attack by the lithium base to give an adduct that subsequently cyclizes to the titled compounds. The reaction of lithiated anilines, nitriles, methanol, and pyrrole failed, presumably due to their inability to deprotonate α -cyano-*o*-tolunitrile.

Isoquinolines constitute an important class of compounds, many of which have significant pharmacological properties.¹ Accordingly, several synthetic methodologies involving classical cyclization reactions or functionalization of a preformed isoquinoline backbone have been reported.² However, the application of such methods to the preparation of isoquinoline-1,3-diamines and 1-alkyl- or 1-arylisoquinoline-3-amines is limited. One of the few reported syntheses of isoquinoline-1,3-diamine involved treating the dinitrile, α -cyano-*o*-tolunitrile, with ammonia at 140 °C for 24 h.³ However, the yield of the 1,3-diamine was only 47%. Treatment of the dinitrile with sodium amide in formamide solvent did not yield isoquinoline-1,3-diamine, but rather produced a mixture of benzylisoquinoline and azachrysene products.⁴ Isoquinoline-1,3-diamine derivatives have also been prepared by the reaction of 2-methyl-4,5-dimethoxybenzo-

nitrile with LDA, followed by treatment with *N,N*-disubstituted cyanamides⁵ and by the amination of 1-halo substituted isoquinoline-3-amines.⁶ However, the yields of the 1,3-diamines in the former are very low (18-20%) and in the latter several steps are needed to prepare the requisite haloisoquinolines from readily available starting materials.

The synthesis of 1-substituted isoquinoline-3-amines has been more actively studied, however, the reported synthetic methods also have severe limitations. For example, Liepa⁷ has prepared several 1-alkyl derivatives of *N*⁶,*N*⁶-dialkylisoquinolin-3-amines by the reaction of nitriles with arylacetic acid tertiary amides in the presence of phosphoryl chloride. However, attempts to prepare 1-alkyl substituted *N*⁶-alkylisoquinolin-3-amines and isoquinolin-3-amine using arylacetic acid secondary and primary amides failed. 1-Alkylisoquinolin-3-amines have been synthesized by the selective reduction and decarboxylation of 3-chloroisoquinoline-4-carboxylic acids.⁸ However, the preparation of the requisite 4-carboxylic acids involved a four step reaction sequence, i.e. condensation of a benzaldehyde with arylacetonitrile to give a 3(2*H*)-isoquinolone,⁹ conversion of the isoquinolone by successive Vilsmeier-Haack¹⁰ acylation and potassium permanganate oxidation under acidic conditions¹¹ into an α -chlorovinylaldehyde, and oxidation of the aldehyde with potassium permanganate under neutral conditions.⁸

We report herein a facile one-step synthesis of a number of different *N*¹-substituted (**3a-e**), and *N*¹, *N*¹-disubstituted isoquinoline-1,3-diamines (**3f-j**) as well as 1-substituted isoquinolin-3-amines (**3k-o**). These amines were prepared by the reaction of α -cyano-*o*-tolunitrile (**1**) with the appropriate lithium amide (**2a-j**), alkylolithium (**2k-n**) or phenyllithium (**2o**) at ambient temperatures for 4 h. The individual yields are listed in Table 1. Noteworthy are the good yields of the sterically demanding 1-*tert*-butyl (72 %) and 1-*sec*-butyl (85 %) derivatives (**3n** and **3m**), respectively. We also found that 1,2-ethanediamine and 1,4-butanediamine react with **1** in the presence of excess *n*-BuLi to give bis-*N*¹-(3-aminoisoquinolin-1-yl)-1,2-ethanediamine (**4**) and bis-*N*¹-(3-aminoisoquinolin-1-yl)-1,4-butanediamine (**5**) in high yields (eq. 1).

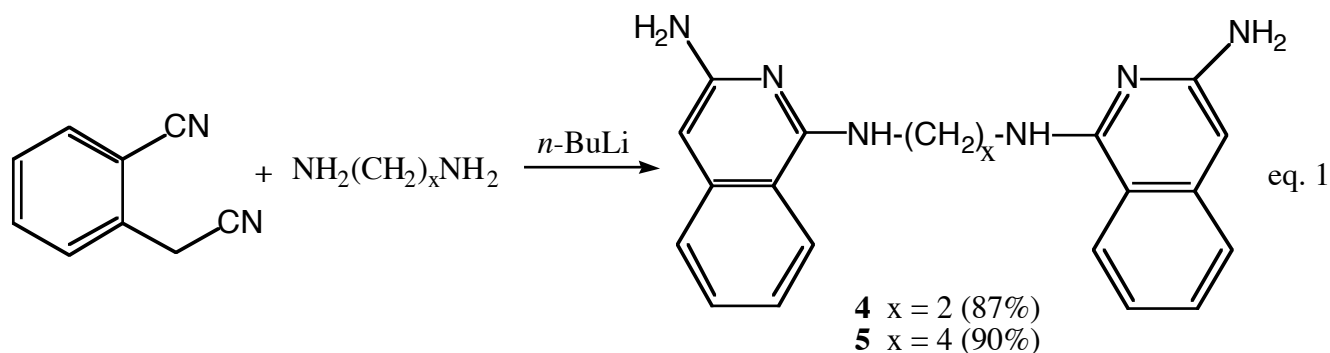
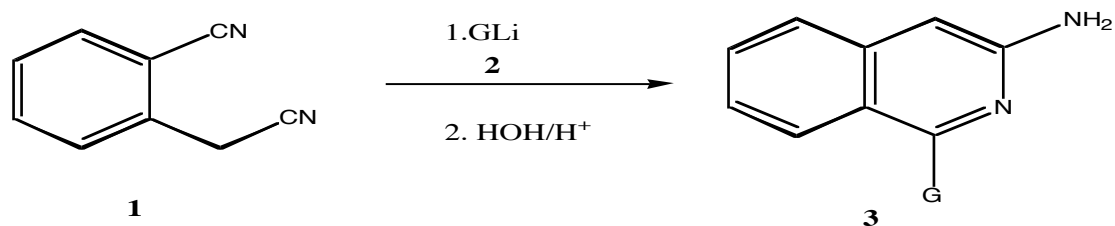


Table 1



Compound	G	Yield (%)
3a	<i>iso</i> -C ₃ H ₇ NH-	89
3b	<i>tert</i> -C ₄ H ₉ NH-	91
3c	<i>n</i> -C ₄ H ₉ NH-	93
3d	(CH ₃) ₂ N(CH ₂) ₂ NH	78
3e	(CH ₃) ₂ N(CH ₂) ₃ NH	67
3f	(<i>n</i> -C ₄ H ₉) ₂ N-	92
3g	(<i>iso</i> -C ₃ H ₇) ₂ N-	40
3h	(C ₆ H ₅ CH ₂)(CH ₃)N	84
3i	pyrrolidinyl	95
3j	piperidinyl	95
3k	CH ₃ -	78
3l	<i>n</i> -C ₄ H ₉ -	88
3m	<i>sec</i> -C ₄ H ₉ -	85
3n	<i>tert</i> -C ₄ H ₉ -	72
3o	C ₆ H ₅ -	68
3p	C ₆ H ₅ NH-	a
3q	(C ₆ H ₅)(CH ₃)N-	a
3r	NCCH ₂ -	a
3s	(CH ₃)(NCCH ₂ CH ₂)N	a
3t	Pyrryl	a
3u	CH ₃ O	a

a. not detected.

The proposed structures for **3a-o** were consistent with their ¹H NMR, ¹³C NMR and IR spectra. For example, NMR analysis of **3a-o** indicated a characteristic singlet in each spectrum that

ranged from 5.98 to 6.76 ppm (C_4 -H), consistent with an isoquinoline ring system.⁷ Moreover, the C_4 -H signal for the 1-alkyl (6.58-6.60 ppm) and 1-phenyl (6.76 ppm) derivatives typically occurred at higher fields than that of the N^1 -alkyl (5.96-6.60) and N^1,N^1 -dialkyl (6.07-6.48 ppm) derivatives. The arrangement of the 1,3-amino group was confirmed by single crystal X-Ray diffractometry of compound (**3b**) from which an ORTEP drawing is shown in Figure 1.

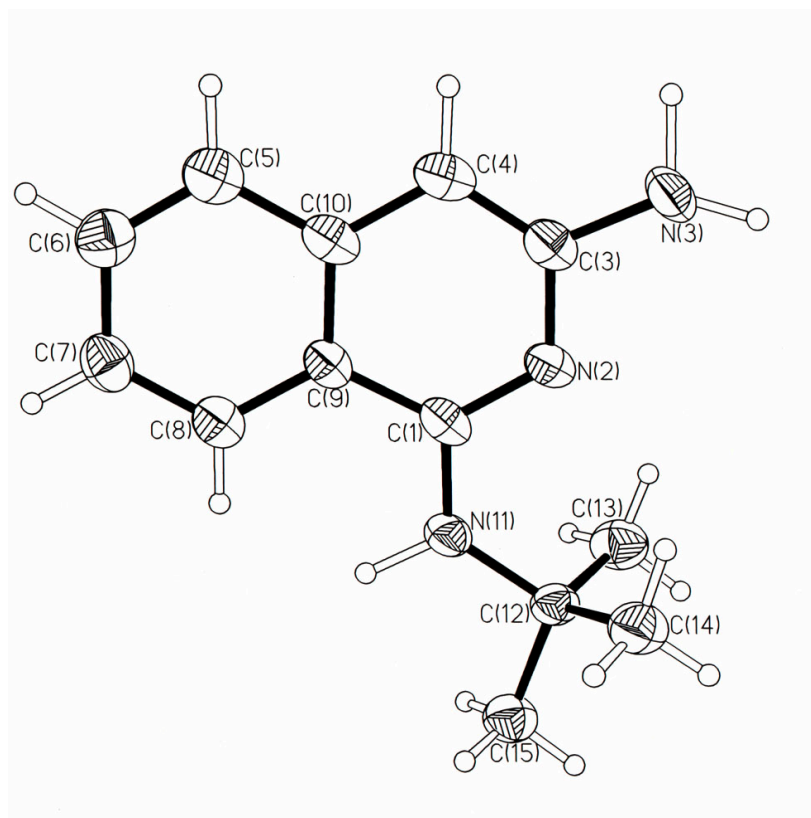


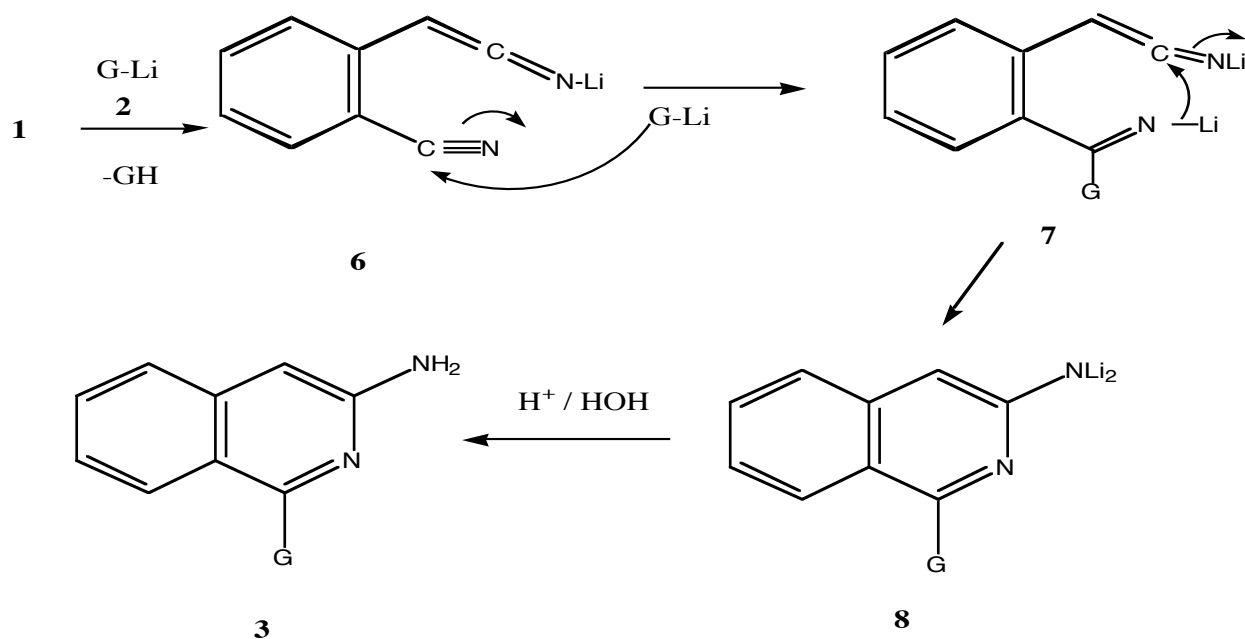
Figure 1 ORTEP drawing of compound (**3b**)

The data in Table 1 show, however, that the reaction of lithiated derivatives of anilines (**2p,q**), acetonitriles (**2r,s**), pyrrole (**2t**), and methanol (**2u**) with **1** failed, even after stirring overnight or when they were carried in the presence of TMEDA or 12-crown-4 ether. The use of elevated temperatures resulted in the formation of inextractable tars.

Scheme 1 depicts a likely mechanism to account for the aforementioned results. As shown, the dinitrile (**1**) is initially deprotonated by the lithiated base (**2**) to give the ketenimine carbanion (**6**). The appropriate lithium amide then adds to the free aromatic cyano group to afford the N -lithiated amidine (G = nitrogen base) or imine (G = alkyl or phenyl) intermediate (**7**), which undergoes cyclization to the N^3,N^3 -dilithiated species (**8**). Upon acidic aqueous quench, **8** is converted to product (**3**). In the previously reported reaction of **1** at 80 °C with sodium amide in formamide solvent,⁴ the dimerized products were thought to occur by various coupling modes involving **1**

and its conjugate base (**6**). That the strong base, sodium amide, did not completely deprotonate **1** to **6** under these conditions probably reflects the low solubility of sodium amide in formamide.

Scheme 1



The use of strong THF-soluble bases (**2a-o**) and the low temperatures reaction conditions employed in this study apparently enable the conversion of **1** to **6** to occur completely before the competing pesky coupling reactions can occur. The failure of the significantly weaker lithiated bases (**2p-u**) as compared to the lithium bases (**2a-o**) to react with **1** under these conditions most likely reflects their inability to convert the dinitrile (**1**) to its ketenimine carbanion (**6**).

In conclusion, a quick one-step synthesis of titled compounds from readily available starting materials has been developed. Furthermore, the sterically demanding *tert*-butyl and isobutyl groups can be added to the 1-position of the isoquinoline ring in good yields.

EXPERIMENTAL

General Data: Melting points were taken on a Mel-Temp capillary apparatus and are uncorrected with respect to stem correction. IR spectra were recorded on a Nicolet Magna-IR™ 550 FTIR spectrophotometer and the ¹H and ¹³C NMR spectra were recorded on a 400 MHz Bruker AVANCE DRX-400 Multi-nuclear NMR spectrometer; chemical shifts were referenced to TMS as internal standard. Elemental analyses were obtained from E + R Microanalytical Laboratories, Inc. The amines and α -cyano-*o*-tolunitrile, which were distilled or recrystallized before use, as

well as phenyllithium and the alkyllithiums (in hexanes), were purchased from Aldrich Chemical Company. The reactions were carried out under an atmosphere of dry O₂-free N₂ via balloon in glassware that had been heated at 125 °C overnight prior to use.

General Procedure. In a flame-dried flask flushed with nitrogen, the lithium amide was prepared by adding 6 mL of *n*-BuLi (15 mmol, 2.5 M in hexane) to a solution of the appropriate amine (15 mmol) in THF (30 mL) at 0 °C. After stirring for 10 min, α -cyano-*o*-tolunitrile (0.71 g, 5 mmol) in THF (15 mL) was added over 5 min. The alkyllithiums (15 mmol) and phenyllithium (1.8 mL of a 1.8 M soln) were added directly to the tolunitrile (1.42 g, 10 mmol) in THF (15 mL) at 0 °C. The stirring was continued for 10 min at 0 °C, allowed to warm to rt then stirred an additional 4 h. The reaction mixture then was quenched with sat. aq. NH₄Cl (30 mL), and the THF evaporated under reduced pressure to give a residue that was extracted with methylene chloride (2 X 20 mL). The combined extracts were washed with brine (2 X 20 mL), dried (Na₂SO₄), and concentrated (rotary evaporator). The remaining mixture was subjected to flash column chromatography (silica gel) using a mixture of hexane/acetone (9:1) as the eluent to give a liquid or solid product. The mp, elemental analyses and NMR spectral data of isolated compounds are given below.

N¹-Isopropylisoquinoline-1,3-diamine (3a): red oil, yield 83 %. IR (nujol) ν_{\max} 3473, 3374, 3054, 1707, 1623.5, 1524, 1454, 1181, 793, 740.5 cm⁻¹. ¹H NMR (acetone-*d*₆) δ 1.29 (d, *J* = 6.8 Hz, 6 H), 4.50 (sept, *J* = 6.8 Hz, 1 H), 4.87 (s, 2 H), 5.96 (s, 1 H), 6.14 (s, 1 H), 6.95 (m, 1 H), 7.28 (m, 2 H), 7.88 (d, *J* = 8.4 Hz, 1 H). ¹³C NMR (acetone-*d*₆) δ 22.4, 42.2, 87.3, 113.0, 120.2, 122.7, 124.6, 129.4, 140.9, 154.7, 155.0. Anal. Calcd for C₁₂H₁₅N₃: C, 71.64; H, 7.46; N, 20.90. Found: C, 71.52; H, 7.36; N, 20.97.

N¹-*tert*-Butylisoquinoline-1,3-diamine (3b): orange solid, mp 103.5-104.5 °C (EtOAc), yield 85 %. IR (KBr) ν_{\max} 3457, 3405, 3364, 2988, 1627, 1567, 1532, 1455, 1409, 1220, 793, 736 cm⁻¹. ¹H NMR (acetone-*d*₆) δ 1.59 (s, 9 H), 4.91 (s, 2 H), 5.81 (s, 1 H), 5.98 (s, 1 H), 6.97 (m, 1 H), 7.29 (m, 2 H), 7.83 (d, *J* = 8.0 Hz, 1 H). Anal. Calcd for C₁₃H₁₇N₃: C, 72.92; H, 7.91; N, 19.12. Found: C, 72.82; H, 7.86; N, 19.18.

N¹-*n*-Butylisoquinoline-1,3-diamine (3c): yellow crystals, mp 179-180 °C (EtOAc), yield 82 %. IR (KBr) ν_{\max} 3477, 3374, 1683.5, 1622.5, 1178.5 cm⁻¹. ¹H NMR (acetone-*d*₆) δ 0.98 (t, *J* = 7.2 Hz, 3 H), 1.47 (m, 2 H), 1.70 (m, 2 H), 3.61 (m, 2 H), 5.24 (s, 2 H), 6.60 (s, 1 H), 7.18 (t, *J* = 7.6 Hz, 1 H), 7.44 (s, 1 H), 7.57 (t, *J* = 7.6 Hz, 1 H), 8.05 (d, *J* = 7.6 Hz, 2 H). Anal. Calcd for C₁₃H₁₇N₃: C, 72.92; H, 7.91; N, 19.12. Found: C, 72.80; H, 7.84; N, 19.23.

***N*¹-(2'-Dimethylaminoethyl)isoquinoline-1,3-diamine (3d)**: oil, yield 78 %. IR (neat) ν_{\max} 3477, 3374, 1683.5, 1622.5, 1178.5 cm^{-1} . ¹H NMR (acetone-*d*₆) δ 2.26 (s, 6 H), 2.60 (t, *J* = 5.6 Hz, 2 H), 3.65 (q, *J* = 5.6 Hz, 2 H), 4.90 (s, 2 H), 5.98 (s, 1 H), 6.45 (s, 1 H), 6.98 (m, 1 H), 7.31 (m, 2 H), 7.79 (d, *J* = 8.0 Hz, 1 H). Anal. Calcd for C₁₃H₁₈N₄: C, 67.80; H, 7.88; N, 24.33. Found: C, 67.85; H, 7.93; N, 24.37.

***N*¹-(3'-Dimethylaminopropyl)isoquinoline-1,3-diamine (3e)**: oil, yield 67 %. IR (neat) ν_{\max} 3357, 3086, 1685, 1569 cm^{-1} . ¹H NMR (acetone-*d*₆) δ 1.83 (m, 2 H), 2.23 (s, 6 H), 2.43 (t, *J* = 5.6 Hz, 2 H), 3.65 (q, *J* = 5.6 Hz, 2 H), 4.97 (s, 2 H), 5.96 (s, 1 H), 6.99 (m, 1 H), 7.18 (s, 1 H), 7.29 (m, 2 H), 7.77 (d, *J* = 8.0 Hz, 1 H). Anal. Calcd for C₁₄H₂₀N₄: C, 68.82; H, 8.05; N, 22.93. Found: C, 68.81; H, 8.13; N, 22.99.

***N*¹,*N*¹-di-*n*-Butylisoquinoline-1,3-diamine (3f)**: tan oil, yield 86 %. IR (nujol) ν_{\max} 3405, 3061, 1614, 1557, 1264, 740, 704 cm^{-1} . ¹H NMR (acetone-*d*₆) δ 0.88 (t, *J* = 7.2 Hz, 6 H), 1.31 (sext, *J* = 7.2 Hz, 4 H), 1.59 (quint, *J* = 7.2 Hz, 4 H), 3.38 (t, *J* = 7.2 Hz, 4 H), 5.02 (s, 2 H), 6.28 (s, 1 H), 7.05 (t, *J* = 8.4 Hz, 1 H), 7.33 (t, *J* = 8.4 Hz, 1 H), 7.38 (d, *J* = 8.4, 1 H), 7.90 (d, *J* = 8.4 Hz, 1 H). Anal. Calcd for C₁₇H₂₅N₃: C, 75.28; H, 9.22; N, 15.50. Found: C, 75.34; H, 9.35; N, 15.58.

***N*¹,*N*¹-Diisopropylisoquinoline-1,3-diamine (3g)**: red oil, yield 40 %. IR (nujol) ν_{\max} 3477, 3374, 1683.5, 1622.5, 1178.5 cm^{-1} . ¹H NMR (acetone-*d*₆) δ 1.13 (d, *J* = 5.6 Hz, 12 H), 3.78 (m, 2 H), 5.05 (s, 2 H), 6.48 (s, 1 H), 7.07 (t, *J* = 8.4 Hz, 1 H), 7.35 (t, *J* = 8.4 Hz, 1 H), 7.40 (d, *J* = 8.4 Hz, 1 H), 8.19 (d, *J* = 8.4 Hz, 1 H). Anal. Calcd for C₁₅H₂₁N₃: C, 74.07; H, 8.64; N, 17.28. Found: C, 74.02; H, 8.62; N, 17.19.

***N*¹-Benzyl-*N*¹-methylisoquinoline-1,3-diamine (3h)**: yellow solid, mp 117-118 °C (EtOAc), yield 63 %. IR (KBr) ν_{\max} 3442, 3420, 3060, 1618, 1556, 1396, 732 cm^{-1} . ¹H NMR (acetone-*d*₆) δ 2.95 (s, 3 H), 4.57 (s, 2 H), 5.10 (s, 2 H), 6.31 (s, 1 H), 7.01 (t, *J* = 5.6 Hz, 1 H), 7.33 (t, *J* = 5.6 Hz, 1 H), 7.36 (m, 3 H), 7.44 (m, 3 H), 7.94 (d, *J* = 8.4 Hz, 1 H). Anal. Calcd for C₁₇H₁₇N₃: C, 77.54; H, 6.51; N, 15.96. Found: C, 77.75; H, 6.60; N, 15.87.

1-(Pyrrolidin-1-yl)isoquinolin-3-amine (3i): brown oil, yield 95 %. IR (nujol) ν_{\max} 3477, 3378, 3050, 1683.5, 1619.5, 1560, 1446, 738, 702 cm^{-1} . ¹H NMR (acetone-*d*₆) δ 1.90 (m, 6 H), 3.70 (m, 4 H), 4.90 (s, 2 H), 6.07 (s, 1 H), 6.94 (m, 1 H), 7.26 (m, 2 H), 8.02 (d, *J* = 8.4 Hz, 1 H). Anal. Calcd for C₁₃H₁₅N₃: C, 73.24; H, 7.04; N, 19.72. Found: C, 73.12; H, 7.06; N, 19.78.

1-(Piperidin-1-yl)isoquinolin-3-amine (3j): yellow oil, yield 95 %. IR (nujol) ν_{\max} 3467, 3374, 1683.5, 1622.5, 1178.5 cm^{-1} . ¹H NMR (acetone-*d*₆) δ 1.62 (m, 2 H), 1.75 (m, 4 H), 3.26 (t, *J* = 5.6 Hz, 4 H), 5.07 (s, 2 H), 6.30 (s, 1 H), 7.06 (t, *J* = 8.0 Hz, 1 H), 7.33 (t, *J* = 8.0 Hz, 1 H), 7.38 (d, *J*

= 8.0 Hz, 1 H), 7.87 (d, $J = 8.0$ Hz, 1 H). ^{13}C NMR (acetone- d_6), δ 24.9, 26.2, 52.7, 92.8, 115.9, 120.8, 125.1, 125.9, 129.4, 141.7, 154.1, 162.0. Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{N}_3$: C, 74.01; H, 7.49; N, 18.50. Found: C, 73.86; H, 7.46; N, 18.59.

1-Methylisoquinolin-3-amine (3k): tan crystals, mp 123-125 °C, yield 78 %. IR (KBr) ν_{max} 3387, 3374, 3050, 1626, 1565, 1452, 1264.5, 741, 705 cm^{-1} . ^1H NMR (acetone- d_6) δ 2.74 (s, 1 H), 5.20 (s, 2 H), 6.58 (s, 1 H), 7.16 (t, $J = 7.6$ Hz, 1 H), 7.20 (t, $J = 7.6$ Hz, 1 H), 7.49 (d, $J = 8.4$ Hz, 1 H), 7.93 (d, $J = 8.4$ Hz, 1 H). Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{N}_2$: C, 75.95; H, 6.33; N, 17.72. Found: C, 75.69; H, 6.36; N, 17.84.

1-*n*-Butylisoquinolin-3-amine (3l): colorless crystals, mp 80.5-81.5 °C (EtOAc), yield 88 %. IR (KBr) ν_{max} 3438, 3326, 1625, 1561, 835, 743 cm^{-1} . ^1H NMR (acetone- d_6) δ 0.97 (t, $J = 7.6$ Hz, 3 H), 1.48 (m, 2 H), 1.79 (m, 2 H), 3.14 (t, $J = 8.0$ Hz, 2 H), 5.19 (s, 2 H), 6.58 (s, 1 H), 7.17 (t, $J = 8.4$ Hz, 1 H), 7.40 (t, $J = 8.4$ Hz, 1 H), 7.50 (d, $J = 8.4$ Hz, 1 H), 7.99 (d, $J = 8.4$ Hz, 1 H). Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.97; H, 8.16; N, 13.87.

1-*sec*-Butylisoquinolin-3-amine (3m): oil, yield 85 %. IR (neat) ν_{max} 3367, 3358, 3067, 1622, 1592, 742 cm^{-1} . ^1H NMR (acetone- d_6) δ 0.87 (t, $J = 7.6$ Hz, 3 H), 1.33 (d, $J = 6.8$ Hz, 3 H), 1.70 (m, 2 H), 3.65 (m, 2 H), 5.24 (s, 2 H), 6.60 (s, 1 H), 7.16 (t, $J = 8.4$ Hz, 1 H), 7.37 (t, $J = 8.4$ Hz, 1 H), 7.52 (d, $J = 8.4$ Hz, 1 H), 8.05 (d, $J = 8.4$ Hz, 1 H). Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2$: C, 75.96; H, 8.05; N, 13.99. Found: C, 77.91; H, 8.11; N, 13.92.

1-*tert*-Butylisoquinolin-3-amine (3n): oil, yield 72 %. IR (nujol) ν_{max} 3476, 3367, 3051, 1624, 1557, 1201, 1149, 991, 864, 827, 748, 694 cm^{-1} . ^1H NMR (acetone- d_6) δ 1.58 (s, 9 H), 5.17 (s, 2 H), 6.60 (s, 1 H), 7.16 (t, $J = 8.4$ Hz, 1 H), 7.37 (t, $J = 8.4$ Hz, 1 H), 7.52 (d, $J = 8.4$ Hz, 1 H), 8.34 (d, $J = 8.4$ Hz, 1 H). Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.94; H, 8.06; N, 13.90.

1-Phenylisoquinolin-3-amine (3o): oil, yield 68 %. IR (nujol) ν_{max} 3465, 3315, 3045, 1624, 1560, 1452, 1363, 1297, 1238, 1184, 1151, 777, 745 cm^{-1} . ^1H NMR (acetone- d_6) δ 5.43 (s, 2 H), 6.76 (s, 1 H), 7.11 (t, $J = 8.4$ Hz, 1 H), 7.49-7.56 (m, 7 H), 7.85 (d, $J = 8.4$ Hz, 1 H). Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.94; H, 5.10; N, 12.99.

***N*'-2-([3-Aminoisoquinolin-1-yl]ethyl)isoquinoline-1,3-diamine (4)**: green solid, mp 280 °C, decomp (EtOAc), yield 87 %. IR (nujol) ν_{max} 3292, 3171, 3064, 1653.5, 1617, 764 cm^{-1} . ^1H NMR (DMSO- d_6) δ 4.06 (s, 4 H), 6.01 (s, 2 H), 6.88 (s, 4 H), 7.16 (t, $J = 7.2$ Hz, 2 H), 7.45 (d, $J = 8.0$ Hz, 2 H), 7.55 (t, $J = 7.2$ Hz, 2 H), 8.26 (d, $J = 8.0$ Hz, 2 H), 9.37 (s, 2H). Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_6$: C, 69.75; H, 5.85; N, 24.40. Found: C, 69.85; H, 5.92; N, 24.37.

***N*¹-2-([3-Aminoisoquinolin-1-yl]butyl)isoquinoline-1,3-diamine (5):** yellow solid, mp 250-252 °C, decomp) (EtOAc) , yield 90 %. IR (KBr) ν_{\max} 3325 (br), 3194, 1645, 1569, 1091, 746 cm^{-1} . ¹H NMR (DMSO-*d*₆) δ 1.96 (s, 4 H), 4.25 (s, 2 H), 6.20 (s, 2 H), 6.85 (s, 4 H), 7.20 (t, *J* = 6.8 Hz, 2 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 7.57 (t, *J* = 6.8 Hz, 2 H), 8.35 (d, *J* = 2 H). Anal. Calcd for C₂₂H₂₄N₆: C, 70.94; H, 6.49; N, 22.56. Found: C, 70.87; H, 6.44; N, 22.43.

X-Ray Single Crystal Analysis of 3b. All data shown in Table 2 were collected on a Nicolet R3m/V diffractometer using the θ -2 θ scan technique, Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), scan speed 3.0-15 deg min⁻¹, scan range 3.5-35.00° and a graphite monochromator. Data were corrected for Lorentz, absorption, and polarization effects. The structures were solved by direct methods using SHELXS-86,¹² the model was refined using full-matrix least-squares methods

Table 2 X-Ray data collection and processing parameters for 3b.

formula	C ₁₃ H ₁₇ N ₃	T (K)	228
crystal dmns, cm ⁻³	0.20 X 0.15 X 0.10	decay, %	4.17
Space group	P2 ₁ /c	Data collected	1363
a (Å)	11.086(1)	Unique reflections	905
b (Å)	10.030(1)	R _{int}	0.064
c (Å)	11.516(2)	Parameters	146
β	105.257(6)	R, R _w	0.064, 0.082
V (Å ³)	1201.7(3)	(Δ/σ)	>0.01
Z-value	4	$\rho_{\max}; \rho_{\min} \text{ e\AA}^{-3}$	0.23; - 0.25
D calc (g-cm ³)	1.4190	GOF	1.77

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