A Facile Synthesis of 3-Methylene-4-aryl-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-ones and 3-Arylmethylene-4,5-dihydro-3*H*-benzo[*b*][1,4]diazepin-2-ylamines[1]

R. Pathak, S. Nag, S. Batra*

Medicinal Chemistry Division, Central Drug Research Institute, PO Box 173, Lucknow 226 001, India
Fax +91(522)2623405; fax +91(522)2623938; E-mail: batra_san@yahoo.co.uk

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Abstract: A simple and convenient synthesis of 3-methylene-4-aryl-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-ones was accomplished by the S_N2 nucleophilic substitution of the acetates of Baylis–Hillman adducts of acrylate with 1,2-phenylenediamines, followed by base-mediated intramolecular cyclization. Similar substrates derived from the Baylis–Hillman adducts of acrylonitrile via Pinner's reaction led to 3-arylmethylene-4,5-dihydro-3*H*-benzo[*b*][1,4]diazepin-2-ylamines in good yields.

Key words: Baylis–Hillman, 1,2-phenylenediamine, diazipine, diazepin-2-ones, diazepin-2-ylamines

A large number of pharmaceutical and biologically active agents incorporate heterocycles as a substructural unit. This has maintained researchers motivation for developing new synthetic strategies with which to achieve the synthesis of heterocyclic architectures, in simple and convenient fashions. In recent times, the derivatives afforded via the Baylis–Hillman reaction have proved to be fascinating precursors for the straightforward construction of biologically relevant heterocyclic systems.[2] This is attributed to the propensity of this robust C–C bond forming reaction to deliver products consisting of highly reactive functional groups. We have been interested in the synthesis of heterocycles containing an exocyclic methylene group, utilizing derivatives of the Baylis–Hillman adduct. In this context, recently we have described the synthesis of α-methylene-δ-valerolactones, 3-methylenepiperidin-2,6-diones and 3-methylene-2-pyrrolidinones in excellent yields.[3] In our continued efforts in this direction, we have now achieved a facile and diversity-oriented synthesis of 3-methylene-4-aryl-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-ones and 3-arylmethylene-4,5-dihydro-3*H*-benzo[*b*][1,4]diazepin-2-ylamines.

The benzo[*b*][1,4]diazepin-2-ones constitute unique structures that exhibit a spectrum of biological activities such as interleukin 1β enzyme inhibition and potassium current blockers, amongst others.[4] A survey of the literature revealed several methods,[5] both in solution and in the solid phase, whereby 1,2-phenylenediamine or its precursor, the 2-nitroaniline, have been successfully employed for the synthesis of this structural motif. In principle, the S_N2 reaction of 1,2-phenylenediamine with the acetyl derivative of the Baylis–Hillman adduct should result in a diamino ester derivative, capable of intramolecular cyclization, to yield the methylene benzo[*b*][1,4]diazepin-2-one. Previously, Chuang and Sharpless described the nucleophilic ring opening of the aziridinium ion with 1,2-phenylenediamine, followed by base-mediated ring closure, to afford the benzo[*b*][1,4]diazepin-2-one.[5a] Furthermore, Kim et al. carried out an S_N2' reaction of 1,2-phenylenediamine with the acetyl derivatives of the Baylis–Hillman adducts to afford the diamino esters, which were cyclized in the presence of acetic acid to yield arylmethylene-benzo[*b*][1,4]diazepin-2-ones in low yields, along with other side products.[5b] Intrigued by these reports, we initiated studies on the synthesis of a range of benzo[*b*][1,4]diazepin-2-ones, possessing an exocyclic methylene moiety, from the Baylis–Hillman adducts. The results of these investigations are described in this communication.

The starting substrates for the study, the acetyl derivatives **1a**–**h** of the Baylis–Hillman adduct, were synthesized following the literature procedure.[6] The S_N2 nucleophilic substitution reaction of 1,2-phenylenediamine with the acetates **1a**–**h** was easily accomplished in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) in a tetrahydrofuran (THF)–water system, leading to the formation of diamino esters **2a**–**h** in excellent yields (Scheme 1). Treatment of these diamino esters with sodium hydride in toluene at 80 °C furnished the desired diazepinones **3a**–**h** in good to excellent yields. In order to make the strategy diversity-oriented, it was envisaged that the substituted 2-nitroanilines could be introduced, instead of the 1,2-phenylenediamine, during the S_N2 nucleophilic substitution. Subsequently the nitro group could be reduced chemoselectively to furnish the amine, which could then be cyclized in the usual fashion. Accordingly, the 2-nitroaniline was treated with the acetyl derivative of the Baylis–Hillman adduct, in the presence of DABCO, in a THF–water system. Unfortunately, this reaction failed to occur even after prolonged reaction time. We reasoned that, probably, the nucleophilicity of the aniline is reduced due to the deactivating effect of the nitro group present in the molecule, leading to the failure of reaction. Thus, in an alternative strategy for the synthesis of the desired substrates, the 2-nitroaniline anion was generated by the treatment of 2-nitroaniline with sodium hydride in anhy-

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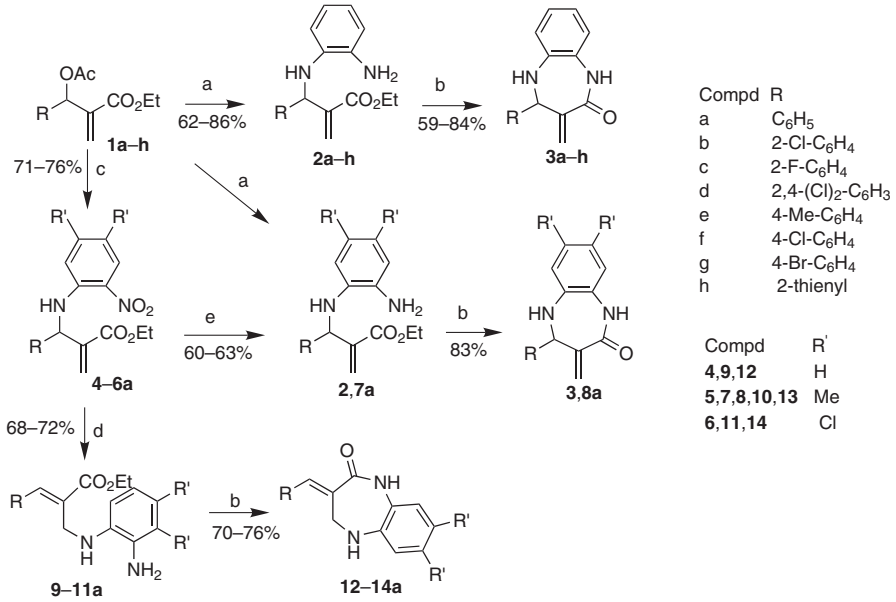
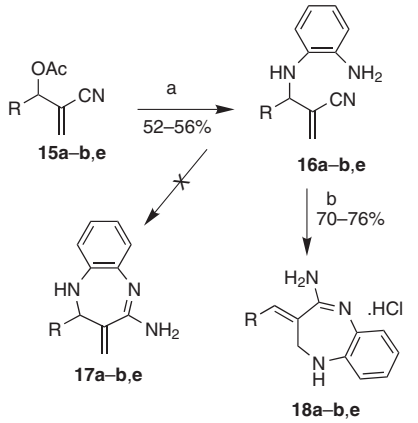


Scheme 1 *Reagents and conditions*: (a) DABCO, 1,2-phenylenediamine or substituted 1,2-phenylenediamine, THF–H_2O (1:1), r.t., 4–5 h; (b) NaH, THF, 80 °C, 2 h; (c) i. Acetate, DABCO, THF, 15 min, ii. (Substituted) 2-nitroaniline, NaH, THF, 15 min, iii. Add i to ii, r.t., 1.5 h; (d) $SnCl_2 \cdot 2H_2O$, MeOH, reflux, 12 h; (e) Zn, HCO_2NH_4, MeOH, r.t., 3 h.

drous THF. This was combined with the acetate **1a**, which had been treated with 4.5 equivalents of DABCO in anhydrous THF for 10 minutes (optimized conditions). Gratifyingly, this reaction was complete in 1.5 hours, and furnished the desired product **4a**. Similarly, the reaction of acetate **1a** with 4,5-dimethyl- and 4,5-dichloro-2-nitroanilines afforded the compounds **5a** and **6a**, respectively.

Reduction of the nitro group of compounds **4**–**6a** was attempted with $SnCl_2 \cdot 2H_2O$. Surprisingly, though the nitro group was reduced to furnish the amino group, a simultaneous rearrangement occurred that resulted in the formation of products **9**–**11a** as the *E*-isomer only. It was presumed that the acidic medium of the reaction mixture may have initiated this unusual rearrangement. In order to validate this assumption, compound **2a** was treated with either hydrochloric or phosphoric acid and found that, in both cases, the rearrangement occurred to yield diaminoester **9a**. Additional chemical evidence for the rearrangement was obtained by treating the compounds **9**–**11a** with sodium hydride to furnish the 3-arylmethylene-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-ones (**12**–**14a**) in good yields. In view of these results, we decided to examine the zinc-mediated reduction of the nitro group in the presence of ammonium formate.[7] We were pleased to observe that, under these conditions, **4a** and **5a** afforded the desired products **2a** and **7a**, respectively, in good yields. These diamino esters were treated with sodium hydride to afford products **3a** and **8a**. In an attempt to improve the yields, we also evaluated an alternate strategy whereby the substituted 2-nitroaniline was first reduced to the corresponding substituted 1,2-phenylenediamine and then subjected to the S_N2 reaction. Hence, the 4,5-dimethyl-2-nitroaniline was hydrogenated in the presence of palladium–carbon to furnish the 4,5-dimethyl-1,2-phenylenediamines in excellent yield. This amine was then subjected to a similar synthetic protocol as described above, to furnish the diaminoester **7a** in 74% yield. Since the difference between the yields was not significant, it was concluded that either strategy could be adopted for the generation of this class of compounds.

Once the objective of obtaining the benzodiazepine-2-ones from the acetyl derivatives of the Baylis–Hillman adduct of acrylate was accomplished, we turned our attention to similar derivatives of acrylonitrile. It was envisaged that the acetyl derivative **15**, upon treatment with 1,2-phenylenediamine, would lead to the formation of the diaminonitrile derivative **16**. The free amino group on the phenyl ring may then attack the cyano moiety, resulting in an intramolecular cyclization to afford the product **17**. To this end, compounds **16a**, **16b** and **16e** were synthesized via S_N2 reactions of 1,2-phenylenediamine on the acetyl derivatives **15a**, **15b** and **15e** (Scheme 2). Unfortunately, the desired cyclization failed in our hands under a range of reaction conditions. Therefore, in order to achieve the desired cyclization, we decided to examine the transformation of the cyano group into the corresponding imidate. In principle, the nucleophilic attack of the amino group on this imidate in situ, should result in the desired benzodiazepinamine **17**. However, though reaction of substrates **16a**, **16b** and **16e** with dry HCl in ethanol led to the isolation of solid products in good yields, the spectral analysis of these compounds indicated that the rearranged products **18a**, **18b** and **18e**, were in fact formed rather than the expected compounds **17**. As discussed above, here too, the acidic medium of the reaction seems to have resulted in the rearrangement of the aniline moiety, leading to the formation of products **18a**, **18b** and **18e**.



Scheme 2 *Reagents and conditions*: (a) 1,2-Phenylenediamine, DABCO, THF–H_2O, r.t., 4–5 h; (b) EtOH–CH_2Cl_2, dry HCl gas, 0 °C, 8 h.

In summary, we have developed a straightforward, convenient and practical synthesis of 3-methylene-4-aryl-1,3,4,5-tetrahydro-benzo[*b*][1,4]diazepin-2-ones with at least two point diversity, utilizing the derivatives of the Baylis–Hillman adducts of acrylates. Similar derivatives, resulting from Baylis–Hillman reaction of acrylonitrile, furnished the 3-arylemethylene-4,5-dihydro-3*H*-benzo[*b*][1,4]diazepin-2-ylamines via tandem conversion of the cyano group into imidates, acid-catalyzed rearrangement, followed by intramolecular cyclization.

Melting points are uncorrected and were determined in capillary tubes on a hot stage apparatus containing silicon oil. IR spectra were recorded using a Perkin Elmer RX I FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on either a 300 or a 200 MHz FT spectrometer, using TMS as an internal standard (chemical shifts in δ values, *J* in Hz). The FAB-MS were recorded on JEOL/SX-102 spectrometers and ES-MS were recorded through a Micromass LCMS system. Elemental analyses were performed on a Carlo Erba 1108 microanalyzer or an Elementar Vario EL *III* microanalyzer. The spectral data for **9a** and **12a** have been published previously.[5b]

Preparation of Compounds 2a–h and 16a,b,e
Prepared following a previously published procedure.[8]

2-[(2-Aminophenylamino)phenylmethyl]acrylic Acid Ethyl Ester (2a)
Yield: 63%; brown oil.

IR (neat): 1711 (CO_2Et), 3397 (NH and NH_2) cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.26 (t, *J* = 7.0 Hz, 3 H, CH_2CH_3), 3.41 (br s, 2 H, NH_2), 4.18 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 5.48 (s, 1 H, H_2C=), 5.96 (s, 1 H, C*H*NH), 6.32 (s, 1 H, H_2C=), 6.55–6.62 (m, 1 H, ArH), 6.71–6.83 (m, 3 H, ArH), 7.30–7.39 (m, 5 H, ArH).

MS (ES+): *m*/*z* = 297.0 [M + H]$^+$.

Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 73.19; H, 6.86; N, 9.11.

2-[(2-Aminophenylamino)(2-chlorophenyl)methyl]acrylic Acid Ethyl Ester (2b)
Yield: 74%; brown oil.

IR (neat): 1705 (CO_2Et), 3431 (NH and NH_2) cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.27 (t, *J* = 8.2 Hz, 3 H, CH_2CH_3), 2.94 (br s, 2 H, NH_2), 4.23 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 5.76 (s, 1 H, H_2C=), 5.91 (s, 1 H, C*H*NH), 6.43 (s, 1 H, H_2C=), 6.50–6.53 (m, 1 H, ArH), 6.67–6.80 (m, 3 H, ArH), 7.22–7.25 (m, 2 H, ArH), 7.35–7.49 (m, 2 H, ArH).

MS (ES+): *m*/*z* = 331.0 [M + H]$^+$.

Anal. Calcd for $C_{18}H_{19}ClN_2O_2$: C, 65.35; H, 5.79; N, 8.47. Found: C, 65.22; H, 5.58; N, 8.43.

2-[(2-Aminophenylamino)(2-fluorophenyl)methyl]acrylic Acid Ethyl Ester (2c)
Yield: 86%; brown oil.

IR (neat): 1713 (CO_2Et), 3399 (NH and NH_2) cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.27 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 3.39 (br s, 2 H, NH_2), 4.12 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 5.75 (s, 1 H, C*H*NH), 5.84 (s, 1 H, H_2C=), 6.40 (s, 1 H, H_2C=), 6.54 (d, *J* = 7.3 Hz, 1 H, ArH), 6.44–6.74 (m, 3 H, ArH), 7.01–7.13 (m, 2 H, ArH), 7.22–7.39 (m, 2 H, ArH).

MS (ES+): *m*/*z* = 315.1 [M + H]$^+$.

Anal. Calcd for $C_{18}H_{19}FN_2O_2$: C, 68.77; H, 6.09; N, 8.91. Found: C, 68.51; H, 5.81; N, 8.77.

2-[(2-Aminophenylamino)(2,4-dichlorophenyl)methyl]acrylic Acid Ethyl Ester (2d)
Yield: 62%; brown oil.

IR (neat): 1714 (CO_2Et), 3365 (NH, NH_2) cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.25 (t, *J* = 7.6 Hz, 3 H, CH_2CH_3), 4.16 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 5.73 (s, 1 H, H_2C=), 5.81 (s, 1 H, C*H*NH), 6.26–6.46 (m, 2 H, H_2C= and ArH), 6.72–6.73 (m, 3 H, ArH), 7.18–7.43 (m, 3 H, ArH).

MS (ES$^+$): *m*/*z* = 365.0 [M + H]$^+$.

Anal. Calcd for $C_{18}H_{18}Cl_2N_2O_2$: C, 59.19; H, 4.97; N, 7.67. Found: C, 58.91; H, 5.16; N, 7.49.

2-[(2-Aminophenylamino)(*p*-tolyl)methyl]acrylic Acid Ethyl Ester (2e)
Yield: 84%; brown oil.

IR (neat): 1711 (CO_2Et), 3402 (NH and NH_2) cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.22 (t, *J* = 7.3 Hz, 3 H, CH_2CH_3), 2.33 (s, 3 H, ArH), 3.34 (br s, 2 H, NH_2), 4.16 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 5.38 (s, 1 H, C*H*NH), 5.88 (s, 1 H, H_2C=), 6.35 (s, 1 H, H_2C=), 6.53 (d, *J* = 7.1 Hz, 1 H, ArH), 6.68–6.79 (m, 3 H, ArH), 7.13 (d, 2 H, *J* = 8.0 Hz, ArH), 7.27 (d, *J* = 8.0 Hz, 2 H, ArH).

MS (ES+): *m*/*z* = 311.1 [M + H]$^+$.

Anal. Calcd for $C_{19}H_{22}N_2O_2$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.30; H, 7.01; N, 8.84.

2-[(2-Aminophenylamino)(4-chlorophenyl)methyl]acrylic Acid Ethyl Ester (2f)
Yield: 62%; brown oil.

IR (neat): 1714 (CO_2Et), 3365 (NH and NH_2) cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.25 (t, *J* = 7.6 Hz, 3 H, CH_2CH_3), 4.16 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 5.73 (s, 1 H, H_2C=), 5.81 (s, 1 H, C*H*NH), 6.26–6.46 (m, 2 H, H_2C= and ArH), 6.72–6.73 (m, 3 H, ArH), 7.18–7.43 (m, 3 H, ArH).

MS (ES+): *m*/*z* = 331.0 [M + H]$^+$.

Anal. Calcd for $C_{18}H_{19}Cl_2N_2O_2$: C, 65.35; H, 5.79; N, 8.47. Found: C, 65.29; H, 5.70; N, 8.45.

2-[(2-Aminophenylamino)(4-bromophenyl)methyl]acrylic Acid Ethyl Ester (2g)
Yield: 75%; brown oil.

IR (neat): 1710 (CO_2Et), 3350 (NH and NH_2) cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.27 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 4.20 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 5.40 (s, 1 H, CHNH), 5.89 (s, 1 H, H_2C=), 6.40 (s, 1 H, H_2C=), 6.54 (d, *J* = 9.1 Hz, 1 H, ArH), 6.72–6.78 (m, 3 H, ArH), 7.29 (d, *J* = 9.0 Hz, 2 H, ArH), 7.47 (d, *J* = 9.0 Hz, 2 H, ArH).

MS (ES+): *m*/*z* = 374.9 $[M + H]^+$.

Anal. Calcd for $C_{18}H_{19}BrN_2O_2$: C, 57.61; H, 5.10; N, 7.47. Found: C, 57.79; H, 5.33; N, 7.48.

2-[(2-Aminophenylamino)(thiophen-2-yl)methyl]acrylic Acid Ethyl Ester (2h)
Yield: 74%; brown oil.

IR (neat): 1711 (CO_2Et), 3401 (NH and NH_2) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 1.26 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 3.45 (br s, 2 H, NH_2), 4.21 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 5.64 (s, 1 H, CHNH), 5.90 (s, 1 H, H_2C=), 6.36 (s, 1 H, H_2C=), 6.58–6.61 (m, 1 H, ArH), 6.74 (s, 3 H, ArH), 6.97 (s, 2 H, ArH), 7.22 (s, 1 H, ArH).

MS (ES+): *m*/*z* = 302.9 $[M + H]^+$.

Anal. Calcd for $C_{16}H_{18}N_2O_2S$: C, 63.55; H, 6.00; N, 9.26. Found: C, 63.76; H, 6.20; N, 8.92.

2-[(2-Aminophenylamino)phenylmethyl]acrylonitrile (16a)
Yield: 52%; brown oil.

IR (neat): 2225 (CN), 3400 (NH and NH_2) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 3.08 (br s, 2 H, NH_2), 5.04 (s, 1 H, CHNH), 6.05 (s, 1 H, H_2C=), 6.11 (s, 1 H, H_2C=), 6.55–6.58 (m, 1 H, ArH), 6.74–6.81 (m, 3 H, ArH), 7.39–7.43 (m, 5 H, ArH).

MS (ES+): *m*/*z* = 250.1 $[M + H]^+$.

Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 76.88; H, 6.21; N, 16.98.

2-[(2-Aminophenylamino)(2-chlorophenyl)methyl]acrylonitrile (16b)
Yield: 63%; brown oil.

IR (neat): 2209 (CN), 3377 (NH and NH_2) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 3.93 (br s, 2 H, NH_2), 5.57 (s, 1 H, CHNH), 6.01 (s, 1 H, H_2C=), 6.11 (s, 1 H, H_2C=), 6.47–6.49 (m, 1 H, ArH), 6.71–6.77 (m, 3 H, ArH), 7.28–7.33 (m, 2 H, ArH), 7.43–7.53 (m, 2 H, ArH).

MS (ES+): *m*/*z* = 284.2 $[M + H]^+$.

Anal. Calcd for $C_{16}H_{14}ClN_3$: C, 67.72; H, 4.97; N, 14.81. Found: C, 67.93; H, 5.04; N, 14.89.

2-[(2-Aminophenylamino)(*p*-tolyl)methyl]acrylonitrile (16e)
Yield: 56%; brown oil.

IR (neat): 2225 (CN), 3411 (NH and NH_2) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 2.37 (s, 3 H, CH_3), 3.39 (br s, 2 H, NH_2), 3.84 (br s, 1 H, CHNH), 5.04 (d, *J* = 3.6 Hz, 2 H, CHNH), 6.04 (d, *J* = 1.0 Hz, 1 H, H_2C=), 6.06 (s, 1 H, H_2C=), 6.55–6.57 (m, 1 H, ArH), 6.74–6.81 (m, 3 H, ArH), 7.10 (d, *J* = 8.0 Hz, 2 H, ArH), 7.31 (d, *J* = 8.0 Hz, 2 H, ArH).

MS (ES+): *m*/*z* = 264.2 $[M + H]^+$.

Anal. Calcd for $C_{17}H_{17}N_3$: C, 77.54; H, 6.51; N, 15.96. Found: C, 77.75; H, 6.40; N, 16.09.

Preparation of 3a–h and 8a; General Procedure
To a stirred solution of either **2a–h** or **7a** (1.0 mmol) in dry THF (10 mL) was added NaH (60% suspension in oil; 0.121 g, 2.5 mmol) and the mixture was heated at reflux for 2 h. On completion, the reaction mixture was extracted with EtOAc (3 × 20 mL) and H_2O (30 mL). The organic layers were pooled, dried over Na_2SO_4 and concentrated to afford a residue, which was purified by silica gel chromatography (hexane–EtOAc, 70:30) to yield the pure products.

3-Methylene-4-phenyl-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-one (3a)
Yield: 76%; light-yellow solid; mp 175–176 °C.

IR (KBr): 1667 (CONH), 3428 (NH) cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 4.01 (s, 1 H, NHCH), 5.18 (s, 2 H, H_2C= and NHCH), 5.99 (s, 1 H, H_2C=), 6.78–6.96 (m, 4 H, ArH), 7.23–7.37 (s, 5 H, ArH), 7.93 (s, 1 H, CONH).

^{13}C NMR ($CDCl_3$ + DMSO-d_6, 50 MHz): δ = 66.4, 121.1, 121.6, 121.7, 122.9, 124.9, 127.3, 128.0, 128.9, 138.4, 141.9, 144.9, 169.6.

MS (ES+): *m*/*z* = 251.0 $[M + H]^+$.

Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.80; H, 5.45; N, 10.87.

4-(2-Chlorophenyl)-3-methylene-4-phenyl-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-one (3b)
Yield: 84%; yellow solid; mp 182–183 °C.

IR (KBr): 1668 (CONH), 3349 (NH) cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 4.18 (s, 1 H, NHCH), 5.43 (s, 1 H, H_2C=), 5.75 (s, 1 H, CHNH), 6.14 (s, 1 H, H_2C=), 6.82–6.84 (m, 1 H, ArH), 6.90–6.97 (m, 2 H, ArH), 7.20–7.23 (m, 2 H, ArH), 7.28 (s, 1 H, ArH), 7.36–7.39 (m, 1 H, ArH), 7.50–7.52 (m, 1 H, ArH), 8.08 (s, 1 H, CONH).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 63.8, 121.5, 121.7, 123.3, 125.1, 125.4, 127.6, 129.3, 129.6, 130.1, 133.2, 138.2, 139.1, 142.6, 169.7.

MS (ES+): *m*/*z* = 285.1 $[M + H]^+$.

Anal. Calcd for $C_{16}H_{13}ClN_2O$: C, 67.49; H, 4.60; N, 9.84. Found: C, 67.67; H, 4.76; N, 9.64.

4-(2-Fluorophenyl)-3-methylene-4-phenyl-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-one (3c)
Yield: 75%: yellow solid; mp 160–162 °C.

IR (KBr): 1660 (CONH), 3316 (NH) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 4.07 (br s, 1 H, NHCH), 5.39 (s, 1 H, H_2C=), 5.63 (s, 1 H, CHNH), 6.10 (s, 1 H, H_2C=), 6.83–6.96 (m, 4 H, ArH), 7.03–7.12 (m, 1 H, ArH), 7.23–7.24 (m, 2 H, ArH), 7.44–7.45 (m, 1 H, ArH), 8.03 (s, 1 H, CONH).

MS (ES+): *m*/*z* = 269.2 $[M + H]^+$.

Anal. Calcd for $C_{16}H_{13}FN_2O$: C, 71.63; H, 4.88; N, 10.44. Found: C, 71.48; H, 5.11; N, 10.25.

4-(2,4-Dichlorophenyl)-3-methylene-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-one (3d)
Yield: 73%; yellow solid; mp 162–164 °C.

IR (KBr): 1650 (CONH), 3411 (NH) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 4.14 (d, *J* = 3.6 Hz, 1 H, NHCH), 5.43 (s, 1 H, H_2C=), 5.70 (d, *J* = 3.6 Hz, 1 H, CHNH), 6.07 (s, 1 H, H_2C=), 6.80–6.84 (m, 1 H, ArH), 6.92–6.98 (m, 3 H, ArH), 7.15–7.20 (dd, J_1 = 1.8 Hz, J_2 = 8.40 Hz, 1 H, ArH), 7.38 (d, *J* = 1.8 Hz, 1 H, ArH), 7.44–7.49 (m, 1 H, ArH), 8.07 (s, 1 H, CONH).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 63.8, 121.7, 121.8, 123.6, 124.9, 125.7, 127.9, 129.9, 130.2, 133.8, 134.7, 137.7, 137.9, 142.3, 169.7.

MS (ES+): *m*/*z* = 319.1 $[M + H]^+$.

Anal. Calcd for $C_{16}H_{12}Cl_2N_2O$: C, 60.21; H, 3.79; N, 8.78. Found: C, 60.50; H, 3.95; N, 8.62.

4-(4-Methylphenyl)-3-methylene-4-phenyl-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-one (3e)
Yield: 74%; white solid; mp 192–194 °C.

IR (KBr): 1665 (CONH), 3421 (NH) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 2.32 (s, 3 H, CH_3), 3.91 (br s, 1 H, CHN*H*), 5.12 (s, 1 H, H_2C=), 5.23 (s, 1 H, C*H*NH), 6.02 (s, 1 H, H_2C=), 6.80–6.91 (m, 2 H, ArH), 6.93–7.08 (m, 1 H, ArH), 7.09–7.12 (m, 2 H, ArH), 7.15–7.29 (m, 3 H, ArH), 8.01 (s, 1 H, CONH).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 21.0, 65.0, 120.5, 121.1, 121.86, 124.3, 126.9, 128.3, 129.0, 136,7, 138.3, 138.9, 145.0, 169.0.

MS (ES+): *m*/*z* = 265.1 $[M + H]^+$.

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.31; H, 5.88; N, 10.39.

4-(4-Chlorophenyl)-3-methylene-4-phenyl-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-one (3f)
Yield: 78%; light-yellow solid; mp 190–192 °C.

IR (KBr): 1658 (CONH), 3298 (NH) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 4.03 (s, 1 H, CHN*H*), 5.26 (s, 2 H, H_2C= and NHC*H*), 5.97 (s, 1 H, H_2C=), 6.82–7.04 (m, 4 H, ArH), 7.31 (s, 4 H, ArH), 8.07 (s, 1 H, CONH).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 66.1, 121.3, 121.7, 122.2, 123.3, 125.2, 128.8, 129.1, 133.8, 138.0, 140.4, 144.5, 169.6.

MS (ES+): *m*/*z* = 285.0 $[M + H]^+$, 287.0 $[M + 3]^+$.

Anal. Calcd for $C_{16}H_{13}ClN_2O$: C, 67.49; H, 4.60; N, 9.84. Found: C, 67.60; H, 4.71; N, 10.01.

4-(4-Bromophenyl)-3-methylene-4-phenyl-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-one (3g)
Yield: 64%; light-yellow solid; mp 196–198 °C.

IR (KBr): 1650 (CONH), 3312 (NH) cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 4.04 (br s, 1 H, CHN*H*), 5.24 (s, 1 H, H_2C=), 5.28 (s, 1 H C*H*NH), 6.00 (s, 1 H, H_2C=), 6.84–7.05 (m, 4 H, ArH), 7.28 (d, *J* = 8.4 Hz, 2 H, ArH), 7.47 (d, *J* = 8.4 Hz, 2 H, ArH), 7.78 (s, 1 H, CONH).

^{13}C NMR ($CDCl_3$ + DMSO-d_6, 50 MHz): δ = 70.1, 125.8, 126.1, 126.3, 126.5, 127.6, 129.7, 133.4, 134.1, 136.5, 143.0, 146.3, 149.5, 174.1.

MS (ES+): *m*/*z* = 329.1 $[M + H]^+$.

Anal. Calcd for $C_{16}H_{13}BrN_2O$: C, 58.38; H, 3.98; N, 8.51. Found: C, 58.54; H, 4.10; N, 8.30.

3-Methylene-4-thiophene-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-one (3h)
Yield: 59%; brown solid; mp 182–184 °C.

IR (KBr): 1666 (CONH), 3418 (NH) cm^{-1}.

^1H NMR ($CDCl_3$ + DMSO-d_6, 200 MHz): δ = 5.06 (br, 1 H, CHN*H*), 5.16 (s, 1 H, H_2C=), (s, 1 H, H_2C=), 5.27 (d, *J* = 4.0 Hz, 1 H, C*H*NH), 5.69 (s, 1 H, ArH), 6.42–6.66 (m, 5 H, ArH and Het-H), 6.93 (d, *J* = 3.0 Hz, 1 H, Het-H), 7.30 (s, 1 H, Het-H), 9.01 (s, 1 H, CONH).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 65.4, 125.4, 126.0, 128.3, 129.4, 129.9, 130.7, 132.3, 133.6; 142.9, 149.3, 152.1, 172.8.

MS (ES+): *m*/*z* = 257.0 $[M + H]^+$.

Anal. Calcd for $C_{14}H_{12}N_2OS$: C, 65.60; H, 4.72; N, 10.93. Found: C, 65.51; H, 4.79; N, 11.12.

2-[2-Amino-4,5-dichlorophenylamino)phenylmethyl]acrylic Acid Ethyl Ester (8a)
Yield: 83%; white solid; mp 138–140 °C.

IR (KBr): 1655 (CONH), 3430 (NH) cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 2.19 (s, 6 H, 2 × CH_3), 3.85 (br s, 1 H, CHN*H*), 5.19 (s, 2 H, NHC*H* and H_2C=), 5.95 (s, 1 H, H_2C=), 6.65 (d, *J* = 2.2 Hz, 2 H, ArH), 7.31–7.42 (m, 5 H, ArH), 7.42 (s, 1 H, CONH).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 19.3, 19.5, 60.8, 122.7, 123.4, 127.1, 127.6, 128.4, 129.2, 131.1, 133.9, 136.4, 142.2, 145.2, 170.3.

MS (ES+): *m*/*z* = 279.2 $[M + H]^+$.

Anal. Calcd for $C_{18}H_{18}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.80; H, 5.45; N, 10.97.

Preparation of 4–6a; General Procedure
To a solution of the appropriate acetate (1.0 mmol) in dry THF (15 mL) was added DABCO (1.02 g, 4.5 mmol) at r.t. and the mixture was stirred for 10 min. During this time, the appropriate 2-nitroaniline (1.0 mmol) was dissolved in dry THF (10 mL) and NaH (0.121 g, 2.5 mmol) was added at r.t. under stirring. The mixture of DABCO and the Baylis–Hillman acetate was added dropwise to the nitroaniline mixture, maintaining dry conditions. The reaction was allowed to proceed at r.t. for 1.5 h. On completion, the reaction mixture was extracted with EtOAc (3 × 20 mL) and H_2O (30 mL). The organic layers were pooled, dried over Na_2SO_4 and concentrated in vacuo to afford a residue, which was purified by silica gel chromatography (hexane–EtOAc, 95:5) to yield the pure products.

2-{[(4,5-Dimethyl-2-nitrophenyl)amino]phenylmethyl}acrylic Acid Ethyl Ester (5a)
Yield: 71%; yellow solid; mp 114–116 °C.

IR (KBr): 1717 (CO_2Et), 3377 (NH) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 1.23 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 2.16 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 4.20 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 5.67 (s, 1 H, C*H*NH), 5.70 (s, 1 H, CHN*H*), 5.82 (s, 1 H, H_2C=), 6.41 (s, 1 H, H_2C=), 6.54 (s, 1 H, ArH), 7.28–7.38 (m, 5 H, ArH), 7.95 (s, 1 H, ArH).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.4, 19.0, 21.2, 58.1, 61.6, 115.5, 125.7, 126.7, 126.9, 127.7, 128.5, 129.4, 130.9, 139.8, 140.27, 142.8, 147.6, 166.2.

MS (ES+): *m*/*z* = 354.9 $[M + H]^+$.

Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.90; H, 6.39; N, 7.67.

2-{[(4,5-Dichloro-2-nitrophenyl)amino]phenylmethyl}acrylic Acid Ethyl Ester (6a)
Yield: 73%; orange solid; mp 114–116 °C.

IR (KBr): 1717 (CO_2Et), 3377 (NH) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 1.27 (t, *J* = 7.4 Hz, 3 H, CH_2CH_3), 4.21 (q, *J* = 7.1 Hz, 2 H, CH_2CH_3), 5.59 (s, 1 H, C*H*NH), 5.63 (s, 1 H, CHN*H*), 5.81 (s, 1 H, H_2C=), 6.45 (s, 1 H, H_2C=), 6.88 (s, 1 H, ArH), 7.37–7.43 (m, 5 H, ArH), 8.30 (s, 1 H, ArH).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.3, 58.6, 61.8, 116.3, 120.1, 127.2, 127.6, 128.1, 128.9, 129.6, 131.6, 138.6, 139.9, 141.6, 142.9, 165.8.

MS (ES+): *m*/*z* = 394.7 $[M + H]^+$.

Anal. Calcd for $C_{18}H_{16}Cl_2N_2O_4$: C, 54.70; H, 4.08; N, 7.09. Found: C, 54.88; H, 3.80; N, 6.90.

Preparation of 9–11a; General Procedure
To a solution of appropriate 2-nitroaniline (1.0 mmol) in MeOH (10 mL) was added $SnCl_2 \cdot 2H_2O$ (1.73 g, 5.0 mmol) and the reaction mixture was heated at reflux with stirring for 12 h in a nitrogen atmosphere. On completion, MeOH was evaporated and the residue was made alkaline with saturated $NaHCO_3$ and then EtOAc (100 mL) was added. The suspension was passed through a bed of celite and the filtrate was partitioned in a separating funnel. The organic layer was separated, dried (Na_2SO_4) and concentrated, to afford a residue which was purified by silica gel chromatography (hexane–EtOAc, 80:20) to yield pure product.

2-{[(2-Amino-4,5-dimethylphenyl)amino]methyl}-3-phenylacrylic Acid Ethyl Ester (10a)
Yield: 72%; brown oil.

IR (neat): 1703 (CO_2Et), 3343 (NH and NH_2) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 1.34 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 2.08 (s, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 3.40 (br s, 2 H, NH_2), 4.08 (s, 2 H, CH_2NH), 4.30 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 6.32 (s, 1 H, ArH), 6.53 (s, 1 H, ArH), 7.37–7.45 (m, 5 H, ArH), 7.90 (s, 1 H, CH_2=).

MS (ES+): *m*/*z* = 325.1 $[M + H]^+$.

Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.04; H, 7.46; N, 8.64. Found: C, 74.19; H, 7.44; N, 8.70.

2-{[(2-Amino-4,5-dichlorophenyl)amino]methyl}-3-phenylacrylic Acid Ethyl Ester (11a)
Yield: 68%; brown oil.

IR (neat): 1710 (CO_2Et), 3418 (NH and NH_2) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 1.32 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 3.40 (s, 2 H, NH_2), 4.07 (s, 2 H, CH_2), 4.27 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 6.45 (s, 1 H, ArH), 6.54 (s, 1 H, ArH), 7.36–7.40 (m, 5 H, ArH), 7.92 (s, 1 H, H_2C=).

MS (ES+): *m*/*z* = 365.2 $[M + H]^+$.

Anal. Calcd for $C_{18}H_{18}Cl_2N_2O_2$: C, 59.19; H, 4.97; N, 7.67. Found: C, 58.95; H, 5.10; N, 7.88

Preparation of 12–14a; General Procedure
These compounds were prepared following the procedure described for **3a**–**h**.[5b]

3-Benzylidene-7,8-dimethyl-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-one (13a)
Yield: 70%; white solid; mp 194–196 °C.

IR (KBr): 1632 (CONH), 3267 (NH) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 2.16 (s, 6 H, 2 × CH_3), 3.85 (br s, 1 H, CHN*H*), 4.10 (s, 2 H, CH_2), 6.55 (s, 1 H, ArH), 6.65 (s, 1 H, ArH), 7.34–7.37 (m, 5 H, ArH), 7.79 (s, 1 H, H_2C=), 7.92 (br s, 1 H, CONH).

MS (ES+): *m*/*z* = 279.2 $[M + H]^+$.

Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.32; H, 6.49; N, 10.22.

3-Benzylidene-7,8-dichloro-1,3,4,5-tetrahydrobenzo[*b*][1,4]diazepin-2-one (14a)
Yield: 76%; white solid; mp 118–120 °C.

IR (KBr): 1657 (CONH), 3374 (NH and NH_2) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 4.12 (s + br s, 3 H, CHN*H* and CH_2), 6.83 (s, 1 H, ArH), 7.07 (s, 1 H, ArH), 7.35–7.39 (m, 5 H, ArH), 7.87 (s, 1 H, H_2C=), 8.54 (s, 1 H, CONH).

^{13}C NMR (DMSO-d_6, 50 MHz): δ = 47.8, 124.3, 126.2, 126.8, 130.3, 132.7, 133.8, 134.6, 137.9, 140.4, 141.8, 145.2, 174.6.

MS (ES+): *m*/*z* = 319.1 $[M + H]^+$.

Anal. Calcd for $C_{18}H_{16}Cl_2N_2O_4$: C, 60.21; H, 3.79; N, 8.78. Found: C, 60.40; H, 4.01; N, 8.55.

Preparation of 2 and 7a; General procedure
To a stirred solution of appropriate 2-nitroaniline (1.0 mmol) in MeOH (10 mL) at r.t. was added zinc powder (0.150 g, 1.5 mmol), followed by HCO_2NH_4 (0.289 g, 3.0 mmol). After the reaction was complete (monitored by TLC), MeOH was evaporated in vacuo and the residue was dissolved in EtOAc (20 mL). This was then passed through a bed of celite and the filtrate was extracted with EtOAC (2 × 20 mL) and washed with H_2O (30 mL). The organic layers were combined, dried over Na_2SO_4 and evaporated to yield the crude product which was purified by silica gel chromatography (hexane–EtOAc, 80:20) to afford the pure compounds.

2-[2-Amino-4,5-dichlorophenylamino)phenylmethyl]acrylic Acid Ethyl Ester (7a)
Yield: 60%; brown oil.

IR (neat): 1748 (CO_2Et), 3407 (NH and NH_2) cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 1.22 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 2.12 (s, 6 H, 2 × CH_3), 3.80 (br s, 1 H, NH), 4.15 (q, *J* = 7.0 Hz, 2 H, CH_2CH_3), 5.37 (s, 1 H, CHNH), 5.90 (s, 1 H, H_2C=), 6.35 (d, *J* = 4.8 Hz, 2 H, H_2C= and ArH), 6.54 (s, 1 H, ArH), 7.29–7.37 (m, 5 H, ArH).

MS (ES+): *m*/*z* = 325.2 $[M + H]^+$.

Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.04; H, 7.46; N, 8.64. Found: C, 73.89; H, 7.65; N, 8.49.

Preparation of 18a–c; General Procedure
Gaseous HCl (~1.5 mmol) was bubbled through a solution of the appropriate nitrile (1.0 mmol) in dry CH_2Cl_2 (10 mL) and EtOH (1.0 mmol, 0.12 mL) at 0 °C. The reaction was kept at 0 °C for 3 h then allowed to warm to r.t. and continued for another 5 h. The excess CH_2Cl_2 was removed under a stream of nitrogen, then dry Et_2O (5 mL) was added to the residue and the flask was allowed to stand at 0 °C for 24 h. The resultant solid was filtered and dried over P_2O_5 to afford the final compounds as the hydrochloride salt.

3-Benzylidine-4,5-dihydro-3*H*-benzo[*b*][1,4]diazepin-2-ylamine Hydrochloride (18a)
Yield: 70%; brown solid, mp 178–179 °C.

IR (KBr): 3408 (NH and NH_2) cm^{-1}.

^1H NMR (CD_3OD, 300 MHz): δ = 3.35 (s, 2 H, CH_2NH), 7.09–7.134 (m, 4 H, ArH), 7.14–7.18 (m, 5 H, ArH), 7.45 (s, 1 H, H_2C=).

MS (ES+): *m*/*z* = 250.0 $[M + H]^+$.

Anal. Calcd for $C_{16}H_{16}ClN_3$: C, 67.25; H, 5.64; N, 14.70. Found: C, 66.96; H, 5.88; N, 14.47.

3-(2-Chlorobenzylidine)-4,5-dihydro-3*H*-benzo[*b*][1,4]diazepin-2-ylamine Hydrochloride (18b)
Yield: 77%; white solid; mp 216–218 °C.

IR (KBr): 3410 (NH and NH_2) cm^{-1}.

^1H NMR (CD_3OD, 300 MHz): δ = 3.33 (s, 2 H, CH_2NH), 7.17–7.20 (m, 4 H, ArH), 7.17–7.20 (m, 6 H, ArH and H_2C=).

MS (ES+): *m*/*z* = 284 $[M + H]^+$.

Anal. Calcd for $C_{16}H_{15}Cl_2N_3 \cdot H_2O$: C, 56.82; H, 5.07; N, 12.42. Found: C, 57.13; H, 4.89; N, 12.35.

3-(4-Methylbenzylidine)-4,5-dihydro-3*H*-benzo[*b*][1,4]diazepin-2-ylamine Hydrochloride (18e)
Yield: 74%; brown solid; mp 199–201 °C.

IR (KBr): 3420 (NH and NH_2) cm^{-1}.

^1H NMR (CD_3OD, 300 MHz): δ = 2.37 (s, 3 H, CH_3), 3.32 (s, 1 H, CH_2NH), 3.78 (d, 2 H, *J* = 4.5 Hz, CH_2NH), 6.85–6.90 (m, 4 H, ArH), 7.12–7.37 (m, 4 H, ArH), 7.64 (s, 1 H, H_2C=).

MS (ES+): *m*/*z* = 264 $[M + H]^+$.

Anal. Calcd for $C_{17}H_{18}ClN_3 \cdot H_2O$: C, 64.25; H, 6.34; N, 13.22. Found: C, 64.38; H, 6.66; N, 12.97.

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