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The reported formation of 5*H*-dibenzo[*b,e*][1,4]diazepin-11(10*H*)-ones in the noncatalyzed, base-promoted double arylation of anthranilamide revisited. Correction of some product structures

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Abstract

The base-promoted reaction of 2-halonitro- or 1,2-dihalobenzenes with anthranilamide reported by Cao, Ma et al. (*Synthesis* **2013**, *45*, 111) was reinvestigated. Some of the products reported, which have been identified as dibenzodiazepinones, are actually benzoxazole derivatives. In this paper, the correct structures of these products were established and confirmed by independent synthesis. For four other products, the supposed structures were found to be incompatible with the dibenzodiazepinones that were synthesized by the reliable method used in this work.

KEYWORDS

benzoxazoles, dibenzodiazepinones, nitro compounds

1 | INTRODUCTION

Working on the synthesis of 5*H*-dibenzo[*b,e*][1,4]diazepin-11(10*H*)-one skeleton by the intramolecular reductive condensation of a nitro group with carboxylic acids, promoted by phosphorus (III) compounds [1], we were interested in other methods leading to such structures. We compared efficiency, generality, and selectivity of them in order to find possible advantages of our approach. Our attention was particularly drawn to the method of the synthesis of diazepinones published by Cao and Ma [2]. The method is based on the base-promoted arylation of anthranilamide by *o*-halonitro- and *o*-dihalobenzenes. The advantages of this reaction are simple starting materials, mild reaction conditions, easy procedure, and reasonable yields. However, we found that reported NMR spectra of some products obtained by that method (Scheme 1, *method a*), and obtained by us previously (*method b*) [1], did not match. For a representative example, 8-chloro-5*H*-dibenzo[*b,e*][1,4]diazepin-11(10*H*)-one (**1a**), obtained by us from nitroacid **2a**, gave a spectrum that was distinctly different from that of the compound (originally numbered as **3g**) [2] claimed to have the same structure. This finding concerns also 8-trifluoromethyl derivative **1b** obtained from **2b** [1] and reported compound numbered as **3e** [2]. Therefore, we decided to try to explain this discrepancy (copies of the NMR spectra of all synthesized compounds, shown side by side with reproduced spectra of the related compounds described in ref [2] can be found in supporting information) (Appendix S1).

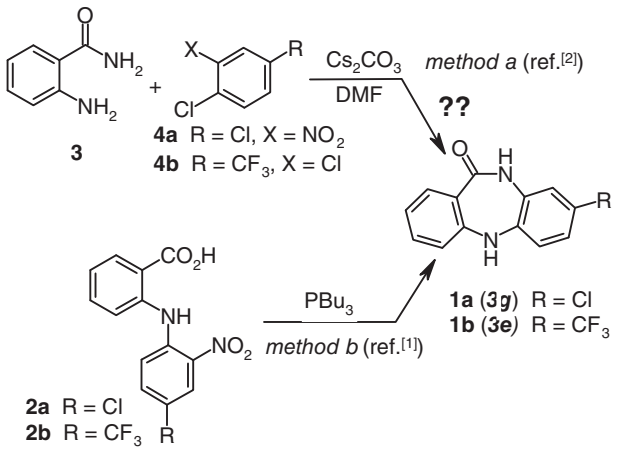
2 | RESULTS AND DISCUSSION

Considering the structure of the starting nitroacids **2** and the chemistry of their cyclization, one could be sure that the structures of **1a** and **1b** are correct. The course of the reaction described in the cited paper seems to be less obvious. To elucidate the problem, we tried to reproduce the reported result. In our hands, the reaction of anthranilamide (**3**) with 2,5-dichloronitrobenzene (**4a**)

carried out under Cs_2CO_3/DMF/150°C conditions afforded a complex mixture from which we isolated less than 5% of a distinct product. The ^1H NMR and ^{13}C NMR spectra of this compound matched exactly those reported for **3g**. Detailed inspection of the spectra and some consideration of possible reaction pathways let us propose a correct structure for compound **3g** having the same molar mass as **1a**. The structure of **3g** was confirmed by independent synthesis (**5a** in Table 1), detailed NMR spectra including most diagnostic ^{15}N spectra [3] (Figure 1), and finally by X-ray measurements (Figure 2) (X-ray computing details can be found in supporting information).

The independent synthesis of **5a** as well as of a few selected (2-aminophenyl)benzoxazoles **5b–e** related to the compounds that were referred to as dibenzodiazepinones [2] was performed by adaptation of a known method [4] in which 2-nitrobenzanilide, obtained by acylation of appropriate *ortho*-aminophenol **7** with 2-nitrobenzoyl chloride, was cyclized without isolation to **8**, then subjected to reduction of the nitro group (Table 1).

On the basis of the NMR spectra, three of the obtained benzoxazoles **5a–c** appeared identical to the compounds described as dibenzodiazepinones **3g**, **3a**, and **3c** in the cited paper [2]. The remaining two (**3e** and



SCHEME 1 The questioned [2] and the reliable [1] route to **1**

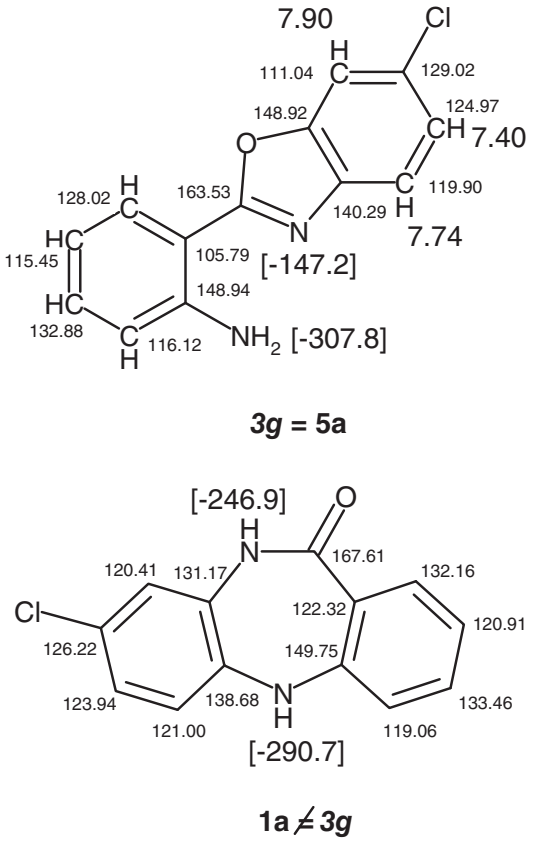
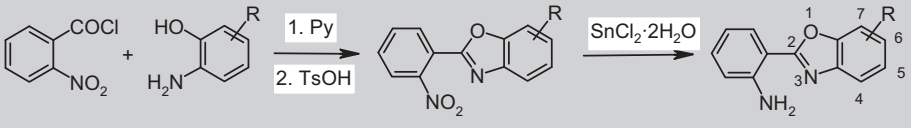


FIGURE 1 Comparison of the NMR assignments for the reported and actual structures of **3g** [2]

TABLE 1 The independent synthesis of (2-aminophenyl)benzoxazoles **5**



6 7a-e 8a-e 5a-e

	2-Aminophenol 7		8		(2-Aminophenyl)benzoxazole 5	
Entry	R in		Isolated yield %		Isolated yield %	R
1	5-Cl	**8a**	55	**5a**	99	6-Cl
2	5-F	**8b**	53	**5b**	89	6-F
3	5-CN	**8c**	21	**5c**	45	6-CN
4	6-Me	**8d**	54	**5d**	98	4-Me
5	5-CF_3	**8e**	54	**5e**	75	6-CF_3

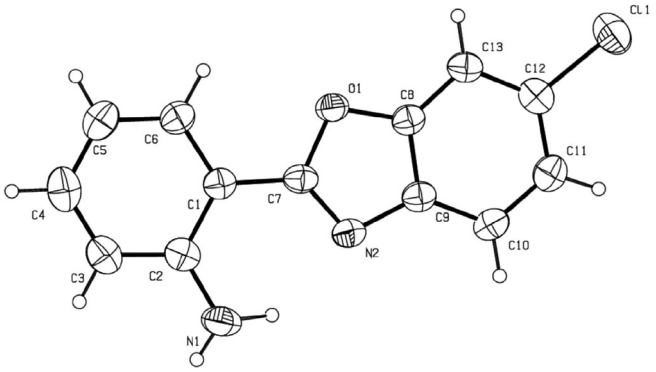
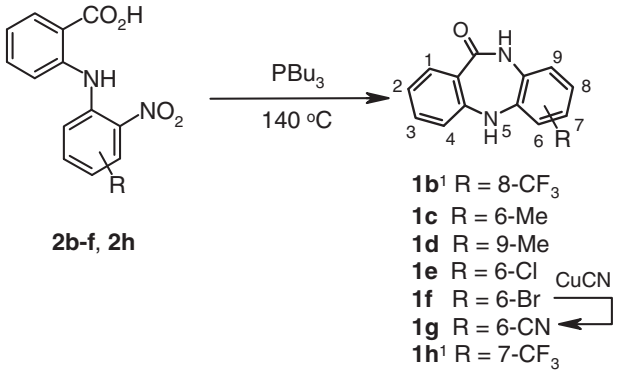


FIGURE 2 ORTEP view of 2-(2-aminophenyl)-6-chlorobenzoxazole (**5a**)



SCHEME 2 The synthesis of dibenzodiazepinones related to the products reported [2]. The synthesis of **1b** and **1h** taken from our previous paper [1]

3f) do not seem to be benzoxazole derivatives as their spectra do not match with respective **5e** and **5d**.

Looking at the structure of the reactants and the reaction conditions (method a, Scheme 1), one might consider the possibility of a different sequence of substitution in which the first more activated leaving group (in this case, chlorine) is replaced by the carboxamide nitrogen anion rather than by the arylamine anion. This would lead to isomeric dibenzazepinones which differ from the expected products by positions of substituents (position 7- vs 8- and 6- vs 9-).

For the elucidation of structures of these and other reported products, a number of appropriate, differently substituted dibenzodiazepinones **1** were obtained by unambiguous cyclization of nitroacids **2** (Scheme 2, includes some earlier results [1]). Their spectra were compared with those reported [2] for the respective products **3b**–**f**.

On this basis, the possible formation of isomeric products for **3e** and **3f** was excluded. Both 6-methyl- (**1c**) and 9-methyl- (**1d**) dibenzodiazepinones turned out to be different from compound **3f**. Possible 7-CF_3 and 8-CF_3 isomeric dibenzodiazepinones, which have been synthesized and described in our previous paper [1] also have inconsistent spectra with a compound reported as **3e** [2].

The spectra of 6-chloro- (**1e**) and 6-cyano- (**1g**) dibenzodiazepinones proved incorrectness of the reported structures of the compounds numbered as **3b** and **3d**. The results of the verification of the reported products [2] are collected in Table 2. Interestingly, the reported special example of the reaction of *N*-methylanthranilamide with 2,3-difluorobenzonitrile that served as evidence of the proposed mechanism (like path a in Scheme 1) gave the expected 10-methyl-11-oxo-10,11-dihydro-5*H*-dibenzo[*b*,*e*][1,4]-diazepine-9-carbonitrile that was proved by single crystal X-ray analysis of the final product but it was the only correctly identified compound [2]. Unfortunately, more extensive discussion of the reaction under consideration is rather difficult as our attempts to reproduce some of the reported results were unsuccessful.

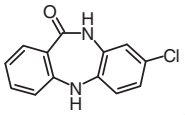
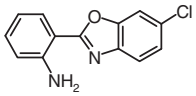
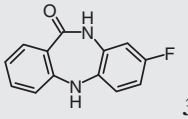
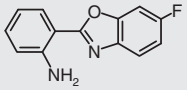
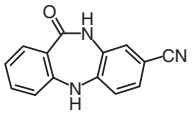
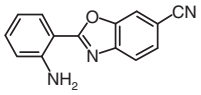
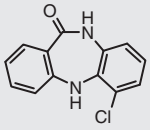
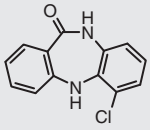
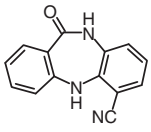
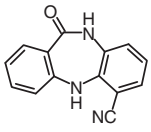
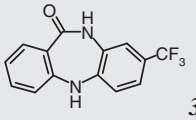
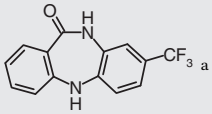
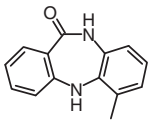
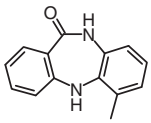
3 | CONCLUSION

The base-promoted reaction of *o*-halonitro- and *o*-dihalobenzenes with anthranilamide, carried out under the reported reaction conditions [2], seems to proceed on several concurrent pathways depending on the starting materials, giving unpredictable or misleading results. Therefore, three of the reported products that have been identified as dibenzodiazepinones are actually aminobenzoxazole derivatives. Four other products showed spectra that are inconsistent with spectra of dibenzodiazepinones synthesized by the reliable method; thus, they are identified and described incorrectly.

4 | EXPERIMENTAL SECTION

Melting points were recorded in open capillary and are uncorrected. The ^{1}H, ^{13}C, and ^{15}N NMR spectra of all compounds studied were measured at temperature 298 K in $CDCl_3$ or deuterated dimethyl sulfoxide (DMSO-d_6) solutions with a Varian vnmrs600 or Varian vnmrs500 using tetramethylsilane (TMS) as the internal standard. Two-dimensional, heteronuclear spectra were recorded with a Varian vnmrs600 aparatus in DMSO-d_6. Mass spectra (EI, 70 eV) were obtained on an AutoSpec Premier (Waters) spectrometer. For ESI+ and ESI− measurements a Maldi SYNAPT G2-S HDMS (Waters) was used. Accurate mass measurements were obtained using magnetic sector mass analyzer (EI) or TOF analyzer (ESI). Silica gel Merck 60 (230–400 mesh) was used for

TABLE 2 Summary of the erroneously reported products [2] (*method a* in Scheme 1)

Declared, incorrect structure (original labels in italics) [2]	Spectral data compatibility	Synthesized and confirmed structure (this work)
 *3g*	Matches with	 **5a**
 *3a*	Matches with	 **5b**
 *3c*	Matches with	 **5c**
 *3b*	Inconsistent	 **1e**
 *3d*	Inconsistent	 **1g**
 *3e*	Inconsistent	 **1b**[a]
 *3f*	Inconsistent	 **1d**

[a]From our previous paper [1].

column chromatography. DMF was dried over CaH_2, distilled, and stored over molecular sieves. All commercial reagents were used without additional purification.

Single-crystal structural data of **5a** were collected by Bruker APEX-II CCD diffractometer. The structural solution and refinement process were done using ShelXL program [5]. The molecular graphics and publication material were generated using PLATON [6] and PublCIF [7] programs.

4.1 | General procedure for the synthesis of benzoxazoles 5a–e

To a solution of appropriate 2-aminophenol **7a**–**e** (33.5 mmol) in dichloromethane (100 mL) was added pyrridine (10 mL). The reaction mixture was cooled to −20°C and 2-nitrobenzoyl chloride (40.0 mmol) was added stepwise. The resulted mixture was allowed to warm up to room temperature and stirred overnight. The volatile components were then removed in vacuo and the residue, crude product, was refluxed with $TsOH{\cdot}H_2O$ (17.0 g, 82 mmol) in toluene with Dean-Stark trap for 2 days. After evaporation of the toluene, the residue was diluted with EtOAc (200 mL), washed with water (2 × 100 mL), dried over Na_2SO_4, and evaporated. The product was isolated using column chromatography (SiO_2, hexane–EtOAc) to obtain 2-nitrophenylbenz oxazoles **8a**–**e**.

2-Nitrophenylbenzoxazole **8** (1.0 mmol) and $SnCl_2{\cdot}2H_2O$ (2.6 g, 10.0 mmol) were stirred in EtOAc (30 mL) at room temperature for 24 h. The mixture was then diluted with EtOAc, washed with water (2 × 50 mL), dried (Na_2SO_4) and the solvent was removed under vacuum. The product (**7a**–**e**) was isolated by column chromatography (SiO_2, hexane–EtOAc).

4.2 | 6-Chloro-2-(2-nitrophenyl) benzoxazole (8a)

Yield: 5.10 g (55%); pale beige solid; mp 112–113°C (lit [8]. 108–109°C). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.48 (dd, J = 8.5, 1.9 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.86–7.92 (m, 2H), 8.02 (d, J = 1.9 Hz, 1H), 8.12 (dd, J = 7.9, 1.0 Hz, 1H), 8.16 (dd, J = 7.5, 1.5 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 112.2, 120.9, 121.8, 125.0, 126.2, 131.1, 131.7, 133.7, 140.4, 149.0, 151.0, 159.5. One carbon signal remains unaccounted for. MS (EI): m/z (%) = 274 (55, $[M]^+$), 204 (62), 202 (85), 140 (61), 134 (72), 104 (100). HRMS (EI): m/z calcd for $C_{13}H_7N_2{}^{35}ClO_3$ $[M]^+$: 274.0145; found: 274.0144.

4.3 | 6-Fluoro-2-(2-nitrophenyl) benzoxazole (8b)

Yield: 4.55 g (53%); beige powder, mp 121°C. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.36 (ddd, J = 9.8, 8.7, 2.4 Hz, 1H), 7.85 (dd, J = 8.7, 2.4 Hz, 1H), 7.90–7.97 (m, 3H), 8.14 (dd, J = 7.8, 1.3 Hz, 1H), 8.19 (dd, J = 7.3, 1.3 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 99.8 (d, J_{FC} = 29 Hz), 113.7 (d, J_{FC} = 25 Hz), 120.0, 121.5 (d, J_{FC} = 10 Hz), 124.9, 131.6, 133.5, 133.6, 138.0 (d, J_{FC} = 2 Hz), 149.0, 150.8 (d, J_{FC} = 16 Hz), 159.4 (d, J_{FC} = 4 Hz), 160.9 (d, J_{FC} = 243 Hz). MS (EI): m/z (%) = 258 (67, $[M]^+$), 213 (23), 186 (93), 134 (71), 124 (75), 104 (100). HRMS (EI): m/z calcd for $C_{13}H_7N_2FO_3$ $[M]^+$: 258.0441; found: 258.0448.

4.4 | 6-Cyano-2-(2-nitrophenyl) benzoxazole (8c)

Yield: 1.86 g (21%); beige powder; mp 204–206°C. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.92–8.00 (m, 3H), 8.08 (d, J = 8.3 Hz, 1H), 8.17–8.20 (m, 1H), 8.23–8.27 (m, 1H), 8.53 (dd, J = 1.5, 0.6 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 108.3, 116.1, 118.5, 119.1, 121.5, 124.6, 129.5, 131.6, 133.4, 133.7, 144.6, 148.6, 149.6, 161.3. MS (EI): m/z (%) = 265 (28, $[M]^+$), 220 (24), 193 (81), 164 (33), 134 (57), 104 (100). HRMS (EI): m/z calcd for $C_{14}H_7N_3O_3$ $[M]^+$: 265.0487; found: 265.0495.

4.5 | 4-Methyl-2-(2-nitrophenyl) benzoxazole (8d)

Yield: 4.57 g (54%); colorless crystals; mp 108°C (lit [9]. mp 104.3–108.8°C). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.55, (s, 3H), 7.25 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.85–7.93 (m, 2H), 8.12 (dd, J = 7.6, 1.2 Hz, 1H), 8.18 (dd, J = 7.6, 1.2 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 19.2, 111.5, 123.3, 127.6, 128.6, 129.1, 133.5, 134.4, 136.0, 136.4, 143.3, 151.7, 153.3, 160.8. MS (EI): m/z (%) = 254 (77, $[M]^+$), 181 (95), 134 (54), 120 (100), 104 (74). HRMS (EI): m/z calcd for $C_{14}H_{10}N_2O_3$ $[M]^+$: 254.0691; found: 254.0697.

4.6 | 2-(2-Nitrophenyl)-6-(trifluoromethyl)benzoxazole (8e)

Yield: 5.57 g (54%); colorless crystals; mp 101–102°C. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.79 (dd, J = 8.4, 1.0 Hz, 1H), 7.89–7.95 (m, 2H), 8.05 (d, J = 8.4 Hz, 1H), 8.14 (dd, J = 7.4, 1.6 Hz, 1H), 8.18 (dd, J = 7.4, 1.6 Hz, 1H), 8.30 (br s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 109.8 (q, J_{FC} = 4 Hz), 119.8, 121.7, 122.7 (q, J_{FC} = 4 Hz), 124.4 (q, J_{FC} = 273 Hz), 125.1, 127.1 (q, J_{FC} = 32 Hz), 131.9, 133.8, 134.0, 144.4 (q, J_{FC} = 1 Hz), 149.1, 150.3, 161.4. MS (EI): m/z (%) = 308 (44, $[M]^+$), 289 (28), 263 (35), 238 (51), 236 (62), 217 (35), 186 (39), 134 (67), 104 (100). HRMS (EI): m/z calcd for $C_{14}H_7N_2F_3O_3$ $[M]^+$: 308.0409; found: 308.0417.

4.7 | 2-(2-Aminophenyl)-6-chlorobenzoxazole (5a)

Yield: 242 mg (99%); pale yellow solid; mp 133–134°C. FT-IR: 3474, 3327, 1623, 1540, 1449 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.66 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 6.88 (dd, J = 8.3, 1.0 Hz, 1H), 7.08 (s, 2H), 7.26 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.40 (dd, J = 8.0, 2.4 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.86 (dd, J = 8.0, 1.4 Hz, 1H), 7.90 (d, J = 2.0 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 106.2, 111.4, 115.9, 116.6, 120.3, 125.4, 128.5, 129.5, 133.3, 140.7, 149.38, 149.39, 164.0. MS (EI): m/z (%) = 246 (51), 244 (100, $[M]^+$), 228 (23), 181 (49). HRMS (EI): m/z calcd for $C_{13}H_9N_2{}^{35}ClO$ $[M]^+$: 244.0403; found: 244.0411.

4.8 | 2-(2-Aminophenyl)-6-fluorobenzoxazole (5b)

Yield: 203 mg (89%); pale yellow solid; mp 125–127°C. FT-IR: 3402, 3368, 3277, 1624, 1546, 1479 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.69 (ddd, J = 8.0, 7.1, 1.1 Hz, 1H), 6.91 (dd, J = 8.3, 0.5 Hz, 1H), 7.09 (s, 2H), 7.25–7.30 (m, 2H), 7.76 (dd, J = 8.4, 2.3 Hz, 1H), 7.79 (dd, J = 8.7, 4.9 Hz, 1H), 7.90 (dd, J = 8.0, 1.4 Hz, 1H). ^{13}C NMR

(125 MHz, DMSO-d_6): δ = 99.2 (d, J_{FC} = 28 Hz), 106.5, 112.6 (d, J_{FC} = 25 Hz), 115.9, 116.5, 120.0 (d, J_{FC} = 10 Hz), 128.3, 133.1, 138.2, 149.0 (d, J_{FC} = 10 Hz), 149.1, 160.2 (d, J_{FC} = 240 Hz), 163.91 (d, J_{FC} = 3 Hz). MS (EI): *m/z* (%) = 228 (100, $[M]^+$), 199 (30). HRMS (EI): *m/z* calcd for $C_{13}H_9N_2FO$ $[M]^+$: 228.0699; found: 228.0690.

4.9 | 2-(2-Aminophenyl)benzoxazole-6-carbonitrile (5c)

Yield: 106 mg (45%); pale yellow solid; mp 209–211°C. FT-IR: 3358, 3278, 3181, 1621, 1544, 1490, 1246 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 6.71 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 7.20 (s, 2H), 7.33 (ddd, J = 8.4, 7.0, 1.4 Hz, 1H), 7.84 (dd, J = 8.4, 1.4 Hz, 1H), 7.90–7.94 (m, 2H), 8.36 (d, J = 1.4 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 105.6, 107.0, 115.3, 116.0, 116.8, 119.4, 120.4, 128.8, 129.6, 134.1, 145.7, 148.4, 150.0, 166.1. MS (EI): *m/z* (%) = 235 (100, $[M]^+$), 206 (21). HRMS (EI): *m/z* calcd for $C_{14}H_9N_3O$ $[M]^+$: 235.0746; found: 235.0757.

4.10 | 2-(2-Aminophenyl)-4-methylbenzoxazole (5d)

Yield: 220 mg (98%); pale beige solid; mp 102–103°C. FT-IR: 3469, 3337, 1625, 1542, 1435, 1326, 1256 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.64 (s, 3H), 6.24 (br s, 2H), 6.77–6.84 (m, 2H), 7.14 (d, J = 7.4 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.26–7.29 (m, 1H), 7.39 (d, J = 8.0 Hz, 1H), 8.07 (dd, J = 8.0, 1.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.5, 107.5, 108.9, 116.2, 116.8, 124.3, 124.8, 128.6, 129.8, 132.1, 141.0, 147.6, 148.9, 162.3. MS (EI): *m/z* (%) = 224 (100, $[M]^+$), 195 (25). HRMS (EI): *m/z* calcd for $C_{14}H_{12}N_2O$ $[M]^+$: 224.0950; found: 224.0949.

4.11 | 2-(2-Aminophenyl)-(5-trifluoromethyl)benzoxazole (5e)

Yield: 208 mg (74%); colorless crystals; mp 114–115°C. FT-IR: 3434, 3330, 2228, 1624, 1535, 1429 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 6.69 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.92 (dd, J = 8.4, 0.8 Hz, 1H), 7.16 (br s, 2H), 7.30 (ddd, J = 8.4, 7.0, 1.7 Hz, 1H), 7.71 (dd, J = 8.4, 1.7 Hz, 1H), 7.91 (dd, J = 8.0, 1.7 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 8.18 (br s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 105.9, 108.7 (q, J_{FC} = 4 Hz), 116.0, 116.7, 120.1, 122.2 (q, J_{FC} = 4 Hz), 124.7 (q, J_{FC} = 272 Hz), 125.6 (q, J_{FC} = 32 Hz), 128.7, 133.8, 144.9 (q, J_{FC} = 1 Hz), 148.7, 149.8, 165.7. MS (EI): *m/z* (%) = 278 (100, $[M]^+$), 249 (14). HRMS (EI): *m/z* calcd for $C_{14}H_9N_2F_3O$ $[M]^+$: 278.0667; found: 278.0667.

4.12 | 6-Methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (1c); typical procedure [1]

In a Schlenk tube, equipped with a teflon plug valve and a magnetic stirring bar, were placed **2c** (544 mg, 2.0 mmol) and PBu_3 (10.0 mL). The vessel was tightly closed, partially immersed in an oil bath placed on a magnetic stirrer hot plate. The reaction mixture was stirred at 140°C for 48 h, then the excess of PBu_3 was removed at reduced pressure (an oil vacuum pump) at ca. 100°C and collected in a cold trap. The residue was then separated on a chromatography column (SiO_2, DCM/MeOH from 50:1 to 10:1).

Yield: 120 mg (26%); pale yellow solid; mp 246–248°C. FT-IR: 3371, 3178, 3047, 1649, 1471 cm^{-1}.^1H NMR (500 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 5.50 (br s, 1H), 6.79–6.83 (m, 2H), 6.89 (t, J = 7.5 Hz, 1H), 6.93 (br d, J = 7.4 Hz, 1H), 7.01 (ddd, J = 8.0, 7.4, 1.0 Hz, 1H), 7.35 (ddd, J = 8.0, 7.4, 1.7 Hz, 1H), 7.82 (br s, 1H), 7.94 (dd, J = 8.0, 1.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.5, 119.6, 119.9, 122.3, 123.3, 123.5, 127.0, 127.4, 129.8, 132.8, 133.6, 138.0, 149.3, 169.0. MS (EI): *m/z* (%) = 224 (100, $[M]^+$), 209 (46), 195 (26). HRMS (EI): *m/z* calcd for $C_{14}H_{12}N_2O_2$ $[M]^+$: 224.0950; found: 224.0951.

4.13 | 9-Methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (1d)

Obtained from **2d** (1088 mg, 4.0 mmol). Yield: 364 mg (41%); pale yellow crystals; mp 250–252°C (dec.). FT-IR: 3316, 3185, 3031, 1639, 1604, 1467 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.41 (br s, 1H), 6.73 (d, J = 7.6 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 6.86–6.95 (m, 2H), 7.01 (t, J = 7.6 Hz, 1H), 7.31–7.35 (m, 1H), 7.35 (br s, 1H), 7.90 (dd, J = 7.8, 1.5 Hz, 1H). ^{13}C NMR (125 MHz, CCl_3): δ = 18.1, 118.2, 119.1, 122.4, 123.2, 125.2, 125.9, 128.0, 129.2, 132.7, 133.6, 140.2, 149.7, 168.8. MS (EI): *m/z* (%) = 224 (100, $[M]^+$), 209 (29), 195 (25). HRMS (EI): *m/z* calcd for $C_{14}H_{12}N_2O$ $[M]^+$: 224.0950; found: 224.0950.

4.14 | 6-Chloro-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11(10*H*)-one (1e)

Obtained from **2e** (293 mg, 1.0 mmol). Yield: 146 mg (60%); colorless crystals; mp 244–246°C. FT-IR: 3343,

3181, 3042, 1643, 1468 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ = 6.92–7.00 (m, 3H), 7.12 (dd, J = 8.1, 0.8 Hz, 1H), 7.15 (dd, J = 7.6, 1.7 Hz, 1H), 7.30 (s, 1H), 7.38 (ddd, J = 8.1, 7.2, 1.7, Hz, 1H), 7.66 (dd, J = 7.6, 1.7 Hz, 1H), 10,10 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6): δ = 120.9, 121.4, 122.5, 124.2, 124.3, 124.4, 125.3, 132.1, 132.9, 133.6, 136.7, 149.6, 168.2. MS (EI): m/z (%) = 246 (29), 244 (64, $[M]^+$), 209 (100). HRMS (EI): m/z calcd for $C_{13}H_9{}^{35}ClN_2O_4$ $[M]^+$: 244.0403; found: 244.0404.

4.15 | 6-Bromo-5*H*-dibenzo[*b*,*e*][1,4] diazepin-11(10*H*)-one (1f)

Obtained from **2f** (1685 mg, 5.0 mmol). Yield: 670 mg (46%); colorless crystals; mp 242–244°C. FT-IR: 3364, 3180, 3041, 1669, 1476 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 6.89 (t, J = 8.0 Hz, 1H), 6.98–7.03 (m, 2H), 7.08–7.12 (m, 2H), 7.31 (dd, J = 7.8, 1.3 Hz, 1H), 7.37–7.42 (m, 1H), 7.67 (dd, J = 7.8, 1.5 Hz, 1H), 10.12 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 114.8, 121.5, 121.6, 122.7, 124.5, 125.0, 128.5, 132.1, 132.9, 133.6, 137.9, 149.5, 168.2. MS (EI): m/z (%) = 290 (52), 288 (53, $[M]^+$), 209 (100), 154 (22). HRMS (EI): m/z calcd for $C_{13}H_9{}^{79}BrN_2O$ $[M]^+$: 287.9898; found: 287.9897.

4.16 | Preparation of 11-oxo-10,11-dihydro-5*H*-dibenzo[*b*,*e*][1,4] diazepine-6-carbonitrile (1g)

To a solution of **1f** (289 mg, 1.0 mmol) in *N*-methylpyrrolidone (15 mL) was added CuCN (108 mg, 1.2 mmol) and the mixture was stirred at 150°C for 48 h. After cooling, the mixture was poured into aqueous NaCl solution (100 mL), extracted with EtOAc (3 × 100 mL). The combined extracts were washed with water (3 × 400 mL) and dried with Na_2SO_4. After evaporation, the residue was subjected to column chromatography (SiO_2, toluene/AcOEt 10:1) to isolate **1 g**.

Yield: 40 mg (17%); colorless crystals; mp 282–283°C. FT-IR: 3328, 3056, 2985, 2225, 1675, 1484 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 7.02–7.08 (m, 2H), 7.15 (t, J = 7.8 Hz, 1H), 7.30 (dd, J = 7.8, 1.2 Hz, 1H), 7.42–7.47 (m, 2H), 7.72 (dd, J = 7.8, 1.5 Hz, 1H), 7.93 (br s, 1H), 10.21 (br s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 103.1, 116.6, 120.8, 122.3, 123.7, 124.0, 126.0, 128.7, 131.9, 132.5, 133.5, 141.3, 148.3, 167.4. MS (EI): m/z (%) = 235 (100, $[M]^+$), 206 (28), 179 (20). HRMS (EI): m/z calcd for $C_{14}H_9N_3O$ $[M]^+$: 235.0746 found: 235.0742.

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DATA AVAILABILITY STATEMENT

Data available in article supplementary material.

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